Structural Features and Reactivity of (sparteine)$PdCl_2$: A Model for Selectivity in an Oxidative Kinetic Resolution of Secondary Alcohols

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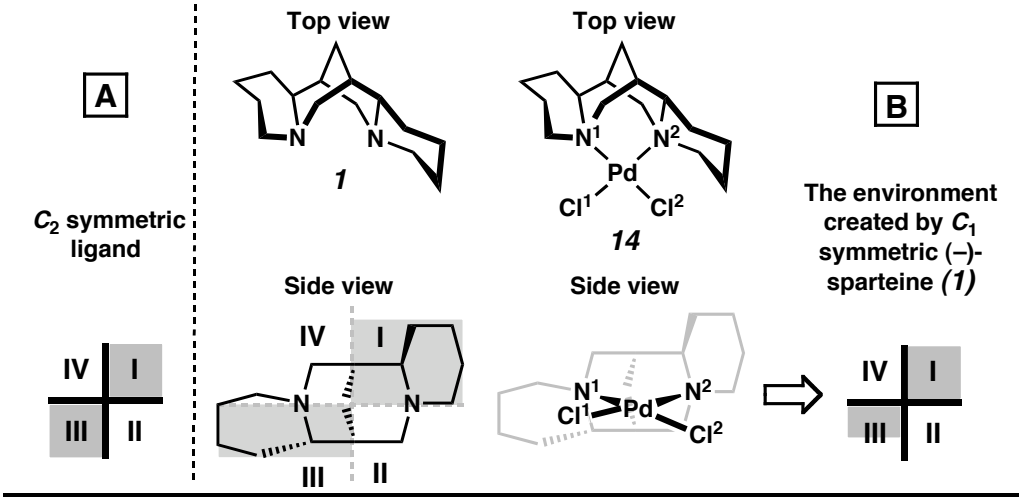
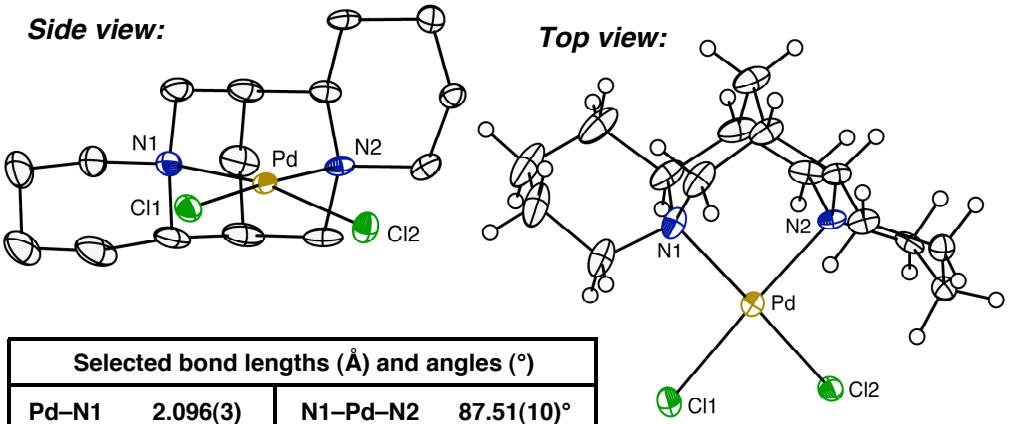
TABLE OF CONTENTS

Materials and Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under a nitrogen atmosphere with freshly distilled solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized via UV and anisaldehyde, potassium permanganate or iodoplatinate staining. ICN silica gel (particle size 0.032-0.063 mm) was used for flash column chromatography. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Mercury 300 spectrometer (at 300 MHz, 75 MHz, and 282 MHz, respectively) and are reported relative to Me_4Si (δ 0.0) for ^{1}H and ^{13}C, and to hexafluorobenzene (δ -162.9) for ^{19}F. Some ^{1}H, ^{13}C, and all ^{2}H and ^{31}P NMR spectra were recorded on a Varian Inova 500 spectrometer (at 500 MHz, 125 MHz, and 121 MHz, respectively) and are reported relative to Me_4Si (δ 0.0) or H_3PO_4 (δ 0.0) for ^{31}P NMR. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift. Data for ^{2}H NMR spectra are reported in terms of chemical shift. Variable temperature NMR experiments were recorded on a Varian Inova 500 spectrometer (at 500 MHz). IR spectra were recorded on a Perkin Elmer BXII spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the California Institute of Technology Mass Spectral Facility.

Selected schemes and figures reproduced from the text.

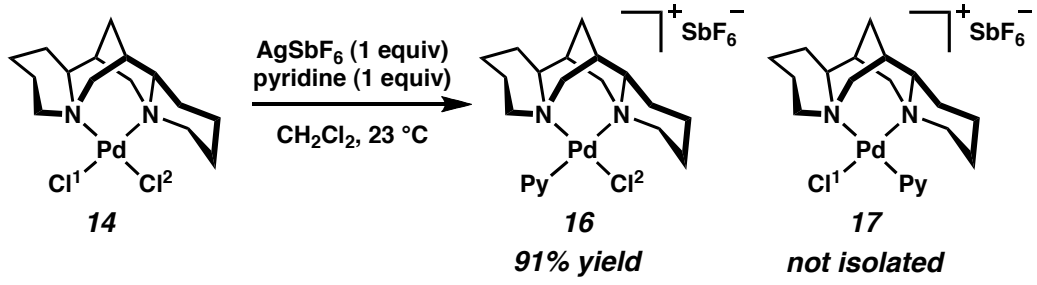
Figure 2.

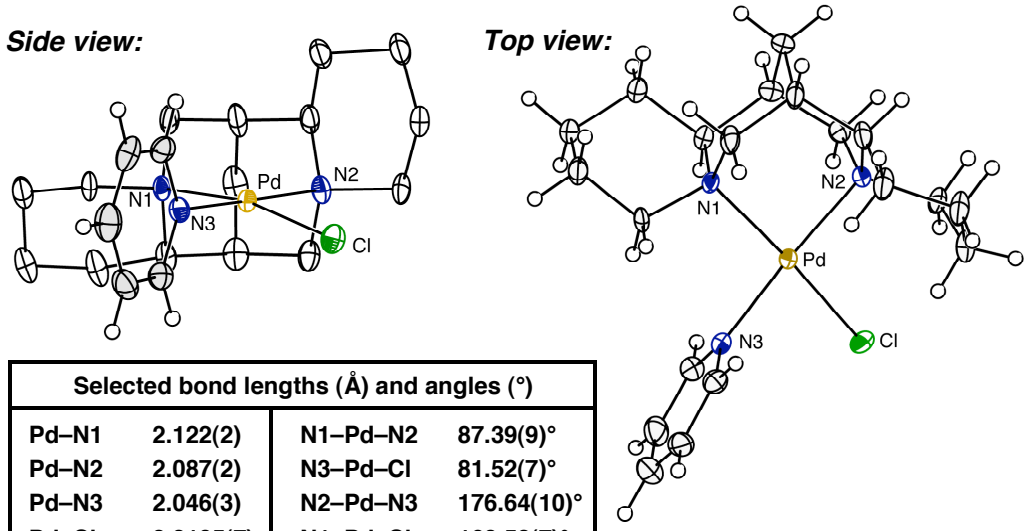




Selected bond lengths (Å) and angles (°)			
Pd–N1	2.096(3)	N1–Pd–N2	87.51(10)°
Pd–N2	2.127(2)	Cl1–Pd–Cl2	83.09(3)°
Pd–Cl1	2.3161(9)	N2–Pd–Cl1	176.24(7)°
Pd–Cl2	2.3150(8)	N1–Pd–Cl2	170.06(8)°
		N1–Pd–Cl1	95.65(8)°
		N2–Pd–Cl2	93.44(7)°
		Σ ∠	705.99°

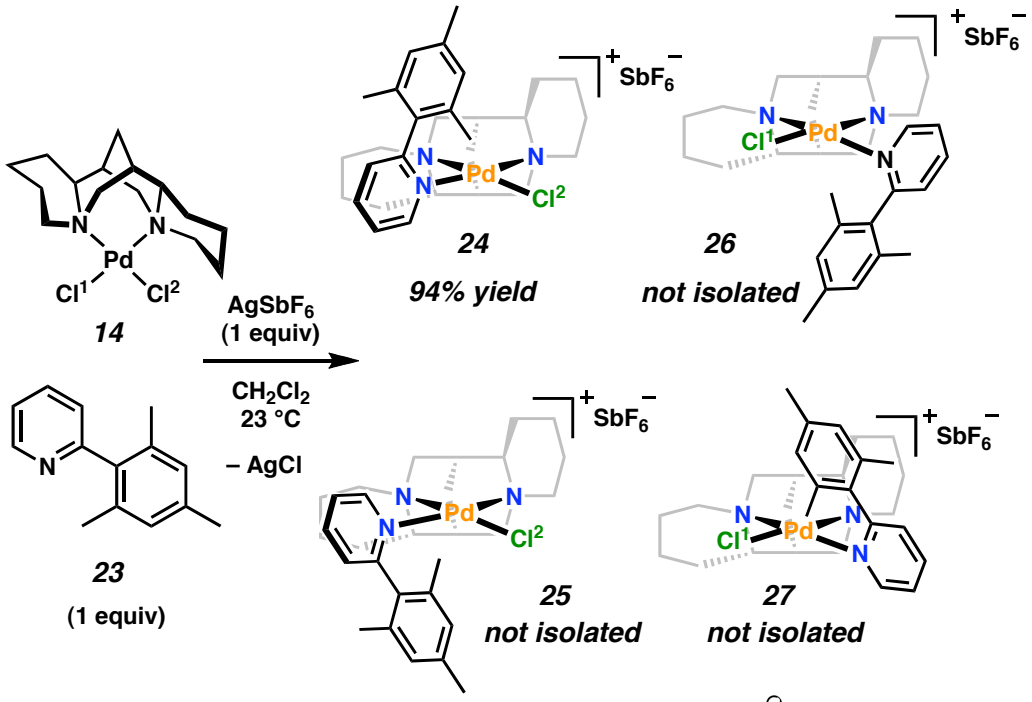
Scheme 2.

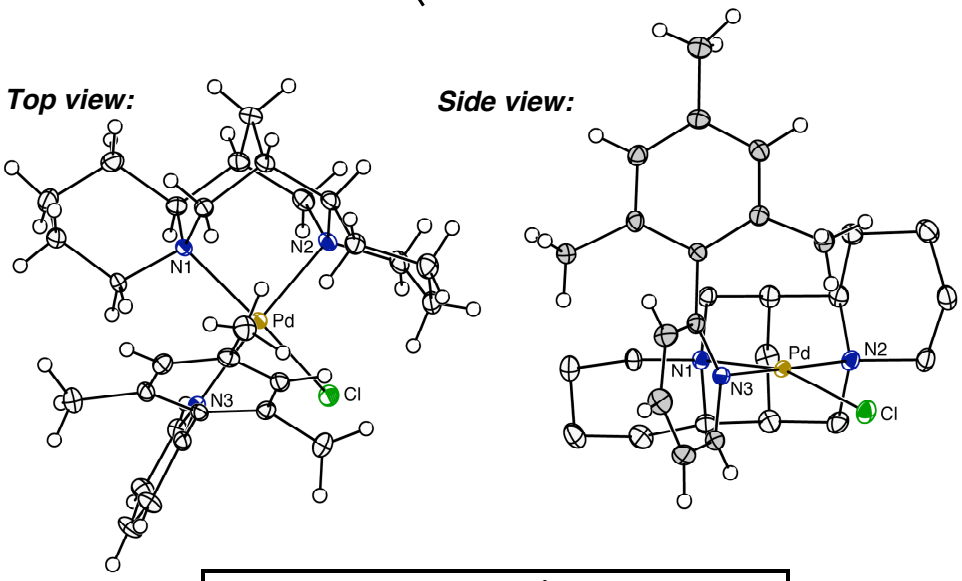




Selected bond lengths (Å) and angles (°)			
Pd–N1	2.122(2)	N1–Pd–N2	87.39(9)°
Pd–N2	2.087(2)	N3–Pd–Cl	81.52(7)°
Pd–N3	2.046(3)	N2–Pd–N3	176.64(10)°
Pd–Cl	2.3105(7)	N1–Pd–Cl	168.52(7)°
		Σ ∠	705.47°

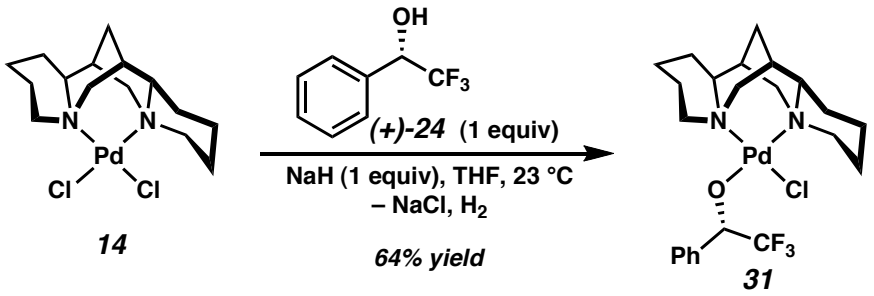
Scheme 5.



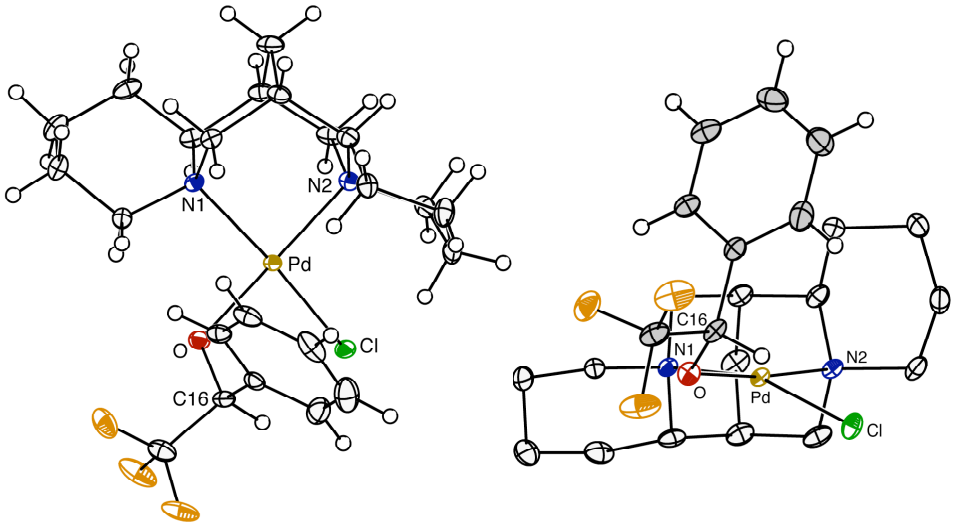


Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1326(14)	N1–Pd–N2	87.48(5)°
Pd–N2	2.0914(14)	N3–Pd–Cl	82.53(4)°
Pd–N3	2.0809(13)	N2–Pd–N3	175.42(5)°
Pd–Cl	2.3345(4)	N1–Pd–Cl	163.51(4)°
		Σ∠	699.45°

Scheme 6.

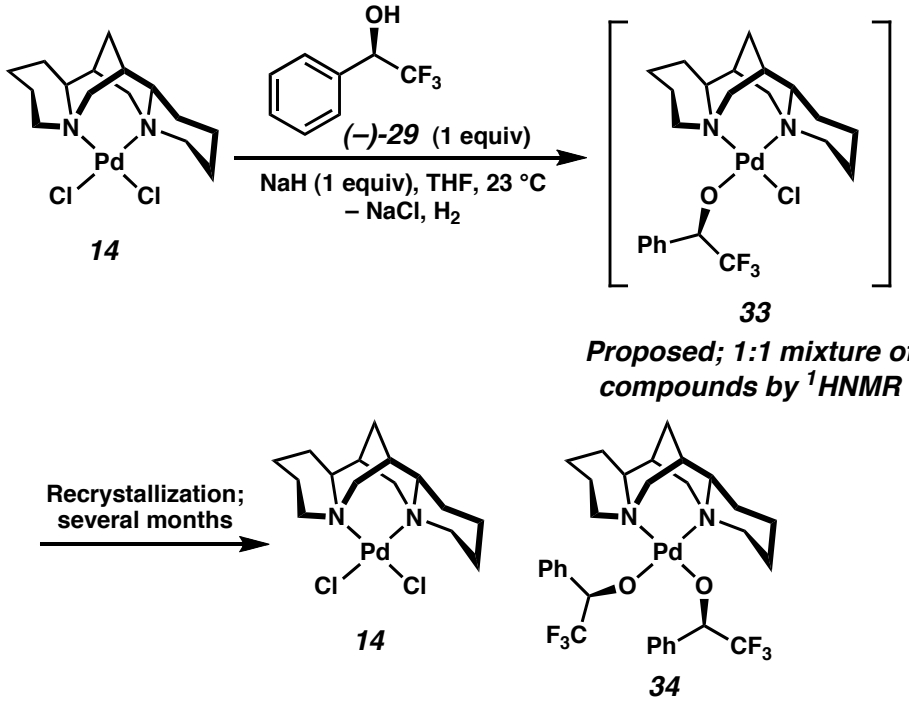


Top view: ***Side view:***

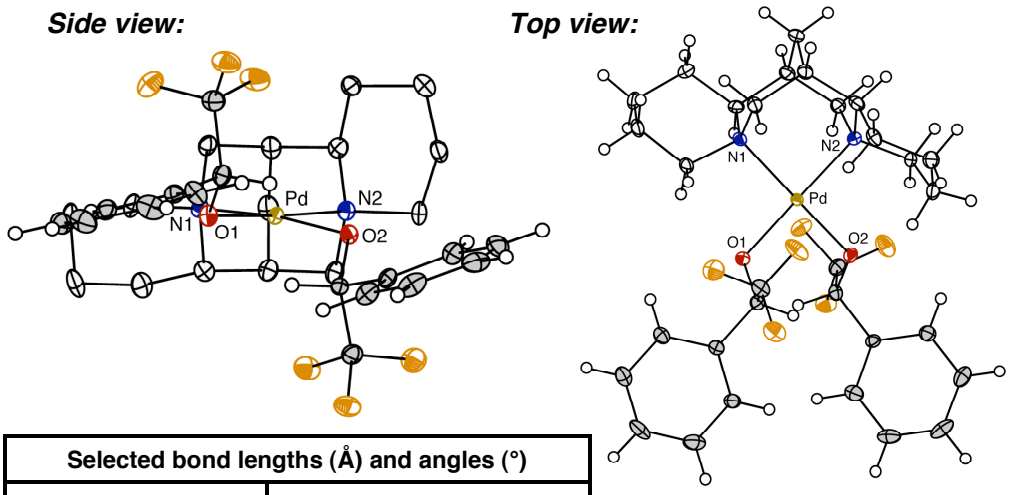


Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1234(17)	N1–Pd–N2	88.07(6)°
Pd–N2	2.0925(16)	O–Pd–Cl	87.71(4)°
Pd–O	2.0012(14)	N2–Pd–O	176.27(6)°
Pd–Cl	2.3316(5)	N1–Pd–Cl	164.59(5)°
		Σ ∠	701.58°

Scheme 8.

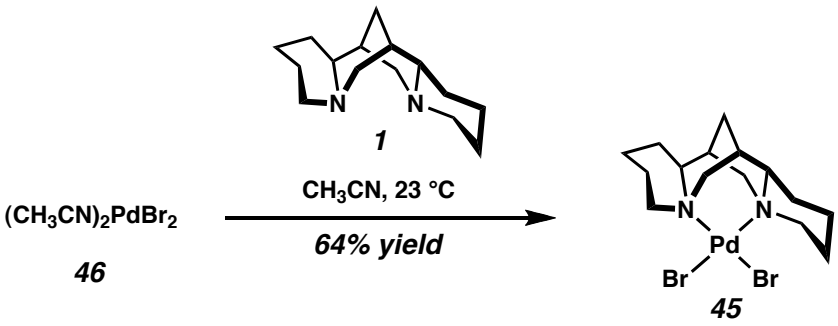


Side view: ***Top view:***



Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1127(15)	N1–Pd–N2	87.57(6)°
Pd–N2	2.1024(16)	O1–Pd–O2	88.53(5)°
Pd–O1	2.0237(13)	N2–Pd–O1	177.26(7)°
Pd–O2	2.0070(13)	N1–Pd–O2	173.14(6)°
		Σ ∠	710.72°

Scheme 9.



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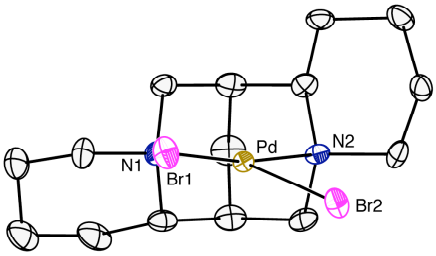

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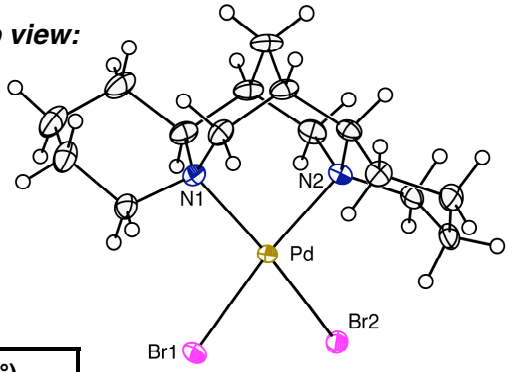
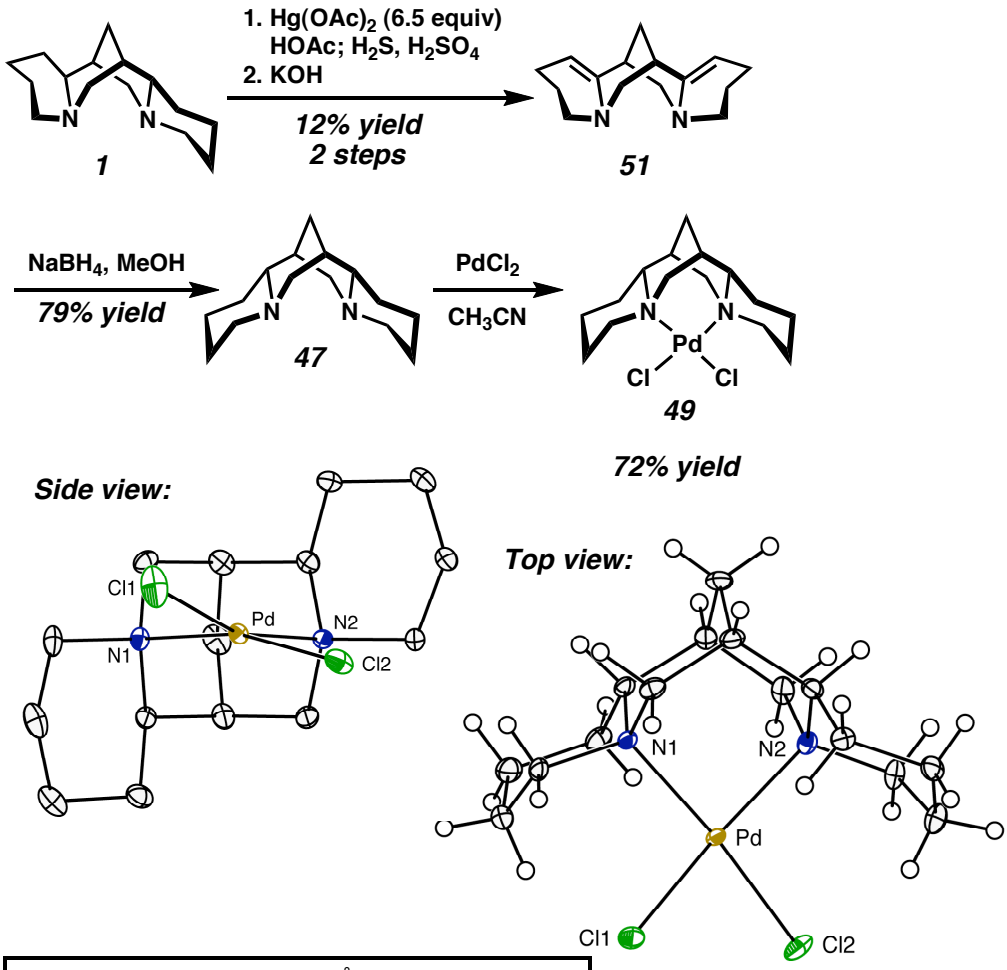


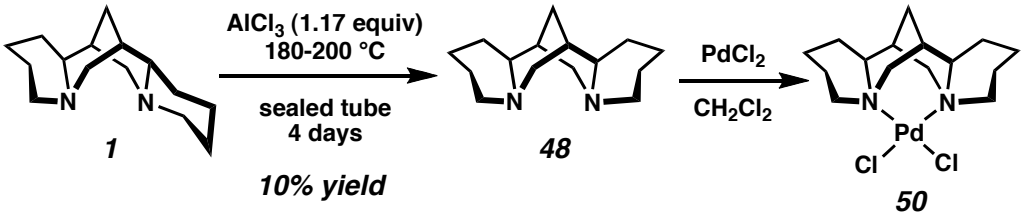
Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1510(18)	N1–Pd–N2	87.43(7)°
Pd–N2	2.1184(16)	Br1–Pd–Br2	84.155(10)°
Pd–Br1	2.4560(3)	N2–Pd–Br1	171.20(5)°
Pd–Br2	2.4474(3)	N1–Pd–Br2	165.96(5)°
		N1–Pd–Br1	96.25(5)°
		N2–Pd–Br2	94.22(5)°
		Σ ∠	699.22°

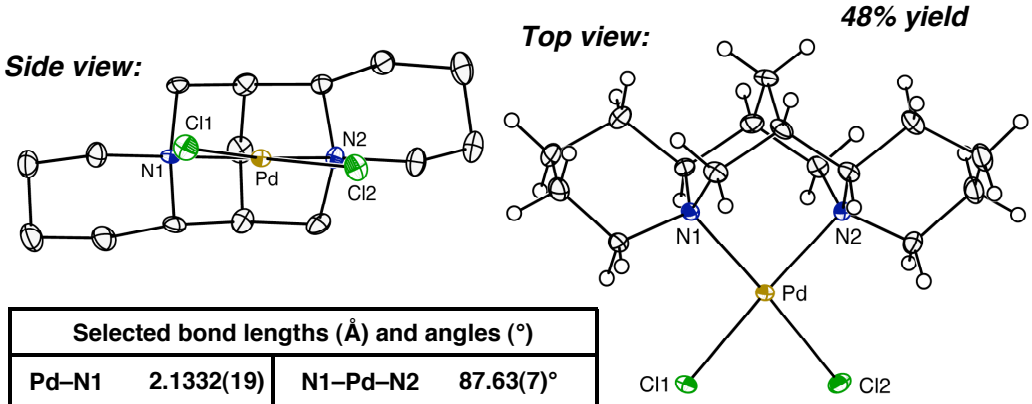
Scheme 10.



Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1091(11)	N1–Pd–N2	87.23(4)°
Pd–N2	2.1271(12)	Cl1–Pd–Cl2	82.205(15)°
Pd–Cl1	2.3275(4)	N1–Pd–Cl2	166.25(4)°
Pd–Cl2	2.3140(3)	N2–Pd–Cl1	163.54(3)°
		Σ∠	693.72°

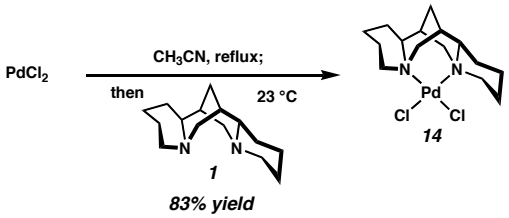
Scheme 11.



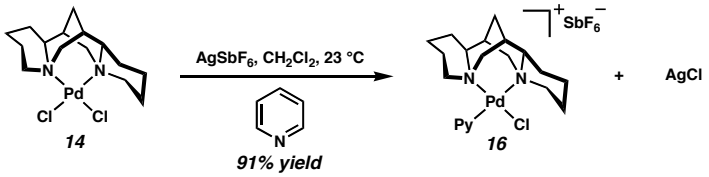


Selected bond lengths (Å) and angles (°)			
Pd–N1	2.1332(19)	N1–Pd–N2	87.63(7)°
Pd–N2	2.1417(19)	Cl1–Pd–Cl2	83.16(2)°
Pd–Cl1	2.3203(6)	N1–Pd–Cl2	174.44(7)°
Pd–Cl2	2.3188(6)	N2–Pd–Cl1	175.87(7)°
		Σ∠	710.68°

The preparation of compounds and the reactions thereof reported in the text.



(sp)PdCl$_2$ (14). $PdCl_2$ (1.5 g, 8.46 mmol, 1.0 equiv) was suspended in CH_3CN (40 mL) and refluxed under N_2 until formation of $(CH_3CN)_2PdCl_2$ was complete, as indicated by the change in color of the suspension form dark purple to yellow-orange. The mixture was allowed to cool to 23 °C at which time (–)-sparteine (**1**) (1.94 mL, 8.46 mmol, 1.0 equiv) was added. Upon stirring of the dark orange-red solution for 1 h under N_2, an orange precipitate formed which was isolated via filtration in air. Trituration of the orange solid from $CHCl_3$ with Et_2O resulted in **14** as a pale orange powder (2.89 g, 7.02 mmol, 83% yield) that was identical by NMR to previously published reports.[1,2] A single crystal suitable for X-ray analysis was grown by slow evaporation from $CDCl_3$ as previously reported.[1]



[(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (16). A Schlenk flask was charged with $AgSbF_6$ (125 mg, 0.364 mmol, 1.0 equiv) and (sp)$PdCl_2$ (**14**) (150 mg, 0.364 mmol, 1.0 equiv). Addition of pyridine (28 μL, 0.364 mmol, 1.0 equiv) via syringe followed immediately by CH_2Cl_2 (10 mL) resulted in nearly instantaneous formation of an orange-yellow solution and pale precipitate. After stirring for 1 h, silver chloride was removed by filtration through Celite in air. Concentration of the filtrate under vacuum yielded **16** as a yellow-orange solid which was recrystallized from acetone and pentane at –20 °C (229 mg, 0.331 mmol, 91% yield). Crystals suitable for X-ray diffraction were grown from acetone layered with pentane at 25 °C. In solution, approx. 10% of a minor component was observed. ^{1}H NMR (300 MHz, acetone-d_6) δ 9.16 (d, J = 4.9 Hz, 1H), 8.89 (d, J = 5.5 Hz, 1H), 8.06 (m, 1H), 7.67-7.59 (comp. m, 2H), 4.69 (dd, J = 12.1, 3.3 Hz, 1H), 4.00 (ddd, J = 13.2, 2.2, 2.2 Hz, 1H), 3.77 (ddd, J = 11.5, 1.7, 1.7 Hz, 1H), 3.24-2.82 (comp. m, 2H), 2.81-2.71 (comp. m, 2H), 2.48 (m, 1H), 2.33-1.48 (comp. m, 17H), 1.10 (m, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 153.7, 152.7, 140.3, 127.7, 126.9, 69.9, 66.6, 66.0, 64.8, 63.7, 49.1, 35.4, 35.1, 31.3, 27.2, 27.0, 26.2, 24.8, 24.1, 21.1; Anal. calc'd for $C_{20}H_{31}ClF_6N_3PdSb$: C, 34.76; H, 4.52; N, 6.08. Found: C, 34.90; H, 4.64; N, 5.79; mp 127-130 °C dec.

Observation of 16 at variable temperatures. **16** (12 mg, 0.017 mmol) was weighed into an NMR tube and dissolved in acetone-d_6 (0.700 μL). 500 MHz ^{1}H NMR spectra were acquired from –60 °C to 45 °C at 15 °C intervals. One major complex, a minor set of peaks, and free pyridine were observable at all temperatures in approximately the same ratios, with significant broadening of the minor set of peaks at 45 °C. Addition of pyridine (1.37 μL, 1.0 equiv) did not significantly change the product distribution. Refer to Figure S1 for the ^{1}H NMR spectra.

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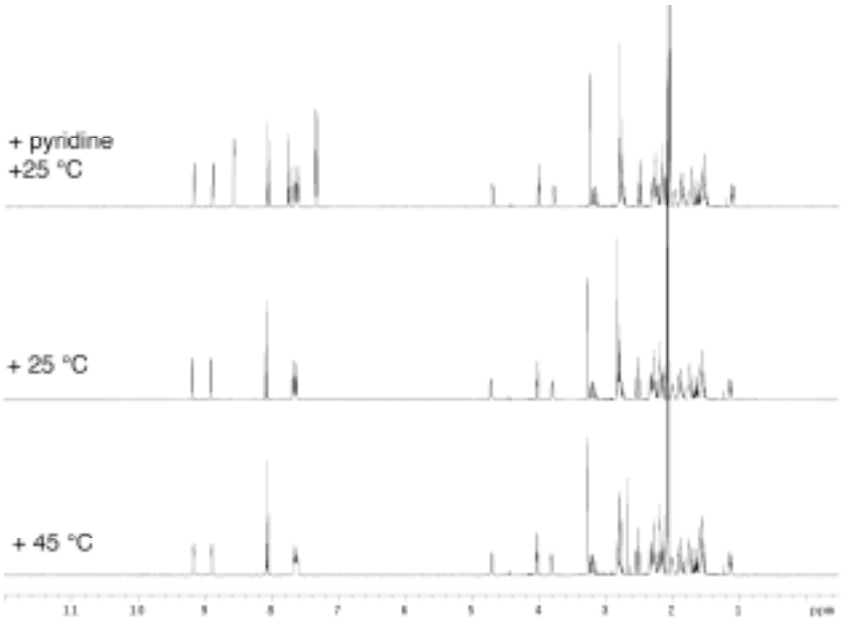
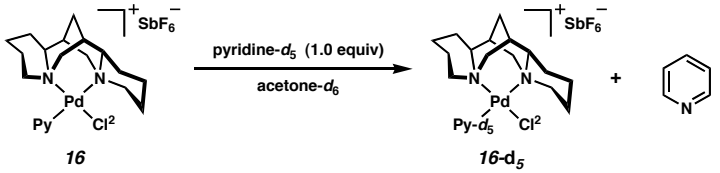
[1] Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 7725-7726.

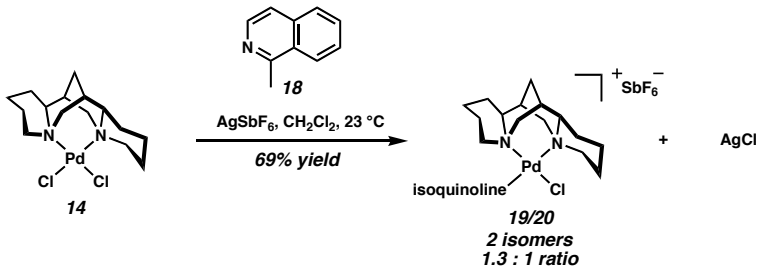
[2] Jensen, D. R.; Pugsley, J. S.; Sigman, M. S. *J. Am. Chem. Soc.* **2001**, *123*, 7475-7476.

Figure S1. ^{1}H NMR spectra of **16** at +45 °C, +25 °C and with 1 equiv added pyridine.



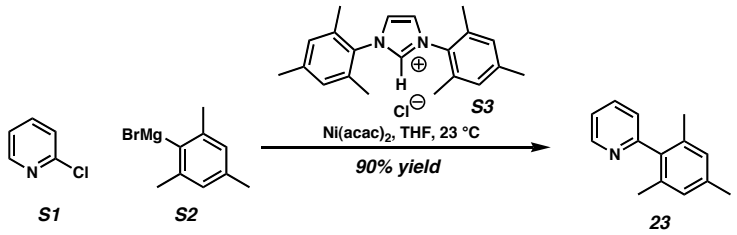


Reaction of 16 with pyridine-d_5. **16** (11.3 mg, 0.016 mmol) was weighed into a sealable NMR tube and dissolved in acetone-d_6 (0.700 mL). A 500 MHz ^{1}H NMR spectrum was acquired at 25 °C. Pyridine-d_5 (1.31 μL, 0.016 mmol, 1 equiv) was added, and another spectrum was acquired. Pyridine-d_5 rapidly became incorporated into the complex (**16-d_5**).

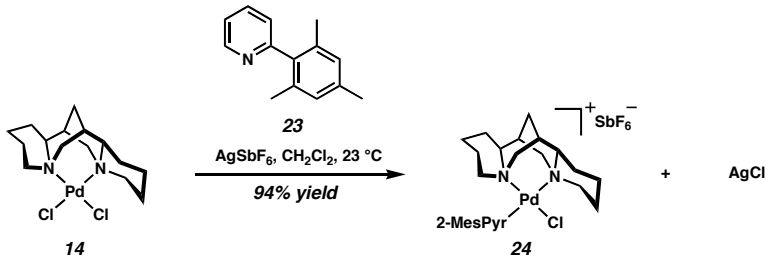


[(sparteine)Pd(2-methylisoquinoline)Cl]$^+$SbF$_6^-$ (19/20). 19/20 was prepared according to the method described for **16** which afforded a yellow-orange solid (375 mg, 0.491 mmol, 69% yield). Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of **19/20**. The ^{1}H NMR spectrum of the crystalline material showed a 1.3:1 mixture of products; the chemical shifts are reported together. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.77 (d, J = 6.6 Hz, 1H), 8.52 (d, J = 6.6 Hz, 1H), 8.27-8.23 (m, 1H), 8.27-8.23 (m, 1H), 7.98-7.77 (comp. m, 4H). 7.98-7.77 (comp. m, 4H), 4.38 (d, J = 12.1 Hz, 1H), 4.36 (d, J = 12.1 Hz, 1H), 4.13 (ddd, J = 13.2, 2.2, 2.2 Hz, 1H), 4.01 (br. d, J = 13.7 Hz, 1H), 3.89 (s, 3H), 3.87-3.76 (comp. m, 2H), 3.87-3.76 (comp. m, 2H), 3.74 (s, 3H), 3.15-0.98 (comp. m, 22H), 3.15-0.93 (comp. m, 22H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.0, 161.8, 142.1, 141.4, 136.1, 136.0, 134.0, 133.9, 130.1, 130.0, 129.5, 128.8, 128.2, 128.1, 126.8, 126.7, 124.2, 123.4, 70.4, 70.4, 67.7, 67.2, 66.32,

66.29, 65.3, 64.3, 63.1, 49.74, 49.68, 35.1, 34.8, 34.7, 31.6, 30.9, 27.52, 27.46, 27.0, 26.8, 25.95, 25.92, 25.7, 24.62, 24.58, 24.56, 24.0, 23.9, 20.9, 20.8; Anal. calc'd for $C_{25}H_{35}ClF_6N_3PdSb$: C, 39.76; H, 4.67; N, 5.56. Found: C, 39.99; H, 4.41; N, 5.64. mp 115-120 °C dec.



2-Mesitylpyridine 23. **23** was prepared by the modified procedure of Hermann et al.[3] A Schlenk tube was charged with nickel(II) acetoacetonate (103 mg, 0.40 mmol, 0.05 mol%), 1,3-bis(2,4,6-trimethylphenyl)-imidazolium chloride (**S3**, 136 mg, 0.40 mmol, 0.05 mol%) and 2-chloropyridine (**S1**, 757 μL, 8.0 mmol, 1.0 equiv) under argon. After addition of THF (8.0 mL), the pale green mixture was stirred for 15 min. Mesityl magnesium bromide (**S2**, 1.83 mL, 2.0 M in THF, 12.0 mmol, 1.5 equiv) was transferred via cannula to the mixture, which immediately became dark brown. After stirring for 45 min, methanol (5 mL) was added and the mixture filtered over Celite and concentrated in vacuo. Flash column chromatography on silica gel (9:1 Hexanes/EtOAc eluent) afforded **23** as a pale pink oil (1.42 g, 7.2 mmol, 90% yield), identical by ^{1}H NMR to that reported.[3]



[(sparteine)Pd(2-mesitylpyridine)Cl]$^+$SbF$_6^-$ (24). **24** was prepared according to the method described for **16** which led to a yellow-orange solid (361 mg, 0.446 mmol, 94% yield). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into an acetone solution of **24**. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.87 (d, J = 5.5 Hz, 1H), 7.94 (ddd, J = 1.6, 7.7, 7.7 Hz, 1H), 7.52 (m, 1H), 7.34 (d, 7.7 Hz, 1H), 7.20 (s, 1H), 7.18 (s, 1H), 4.41 (d, J = 11.0 Hz, 1H), 3.79 (d, J = 12.1 Hz, 1H), 3.61 (ddd, J = 12.6, 2.2, 2.2 Hz, 1H), 2.78-1.13 (comp. m, 23H), 2.42 (s, 3H), 2.21 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 162.1, 154.9, 141.2, 139.9, 139.5, 135.5, 134.4, 130.3, 129.6, 129.4, 125.7, 70.1, 67.3, 65.3, 64.8, 64.0, 48.3, 34.8, 34.3, 28.9, 27.3, 27.0, 25.2, 24.6, 23.9, **22**.2, 21.4, 21.3, 20.6; Anal. calc'd for $C_{29}H_{41}ClF_6N_3PdSb$: C, 43.04; H, 5.11; N, 5.19. Found: C, 43.08; H, 4.99; N, 5.02. mp 140-145 °C dec.

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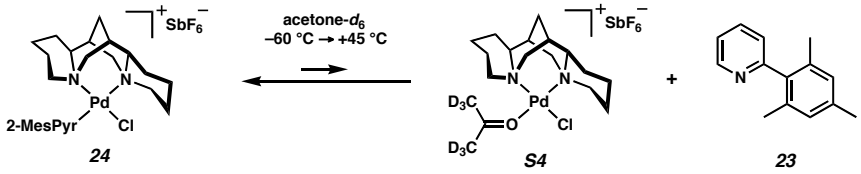
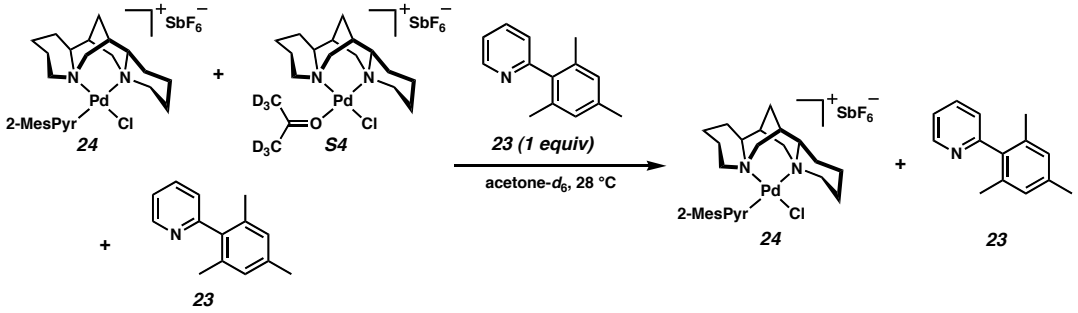
[3] Boehm, V. P. W.; Weskamp, T.; Gstoettmayr, C. W. K.; Hermann, W. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 1602-1604.

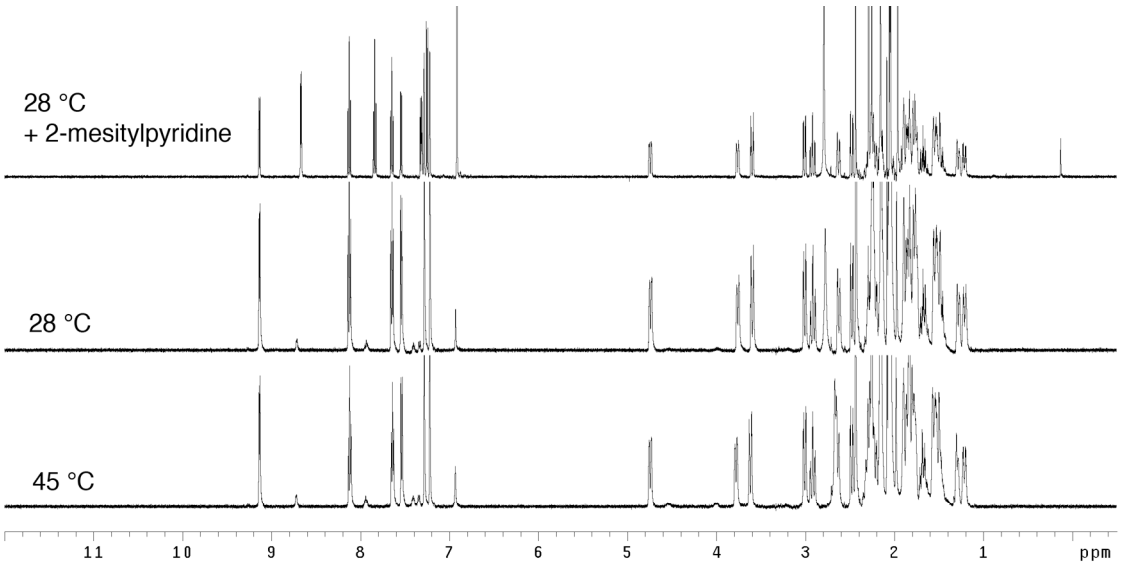


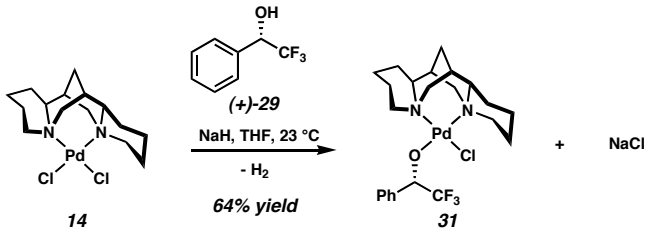
Observation of 24 at variable temperatures. 24 (12 mg, 0.015 mmol) was weighed into an NMR tube and dissolved in acetone-d_6 (0.700 μL). 500 MHz ^{1}H NMR spectra were acquired from –60 °C to +45 °C at 15 °C intervals. One major species and a minor set of peaks were observable at all temperatures. The minor set of peaks increased from 3% at –60°C to 10% at +45°C. We attribute the minor set of peaks to an acetone-ligated cation and free 2-mesitylpyridine. Refer to Figure S1A.



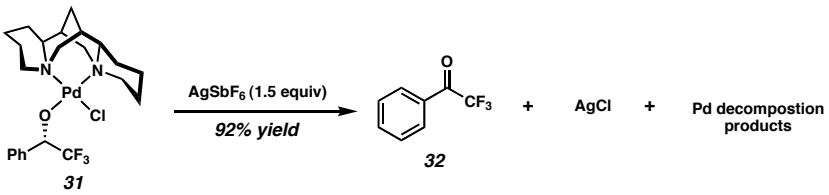
Reaction of 24 and S4 with 2-mesitylpyridine (23). 24 (5.2 mg, 0.0064 mmol) was weighed into a sealable NMR tube and dissolved in acetone-d_6 (0.700 mL). A 500 MHz ^{1}H NMR spectrum was acquired. 2-Mesitylpyridine (**23**, 1.3 mg, 0.0064 mmol, 1 equiv) was added. A 500 MHz ^{1}H NMR spectra was acquired showing disappearance of **S4**. Refer to Figure S1A.

Figure S1A. ^{1}H NMR spectra (500 MHz, acetone-d_6) of **24** at 28 °C and 45 °C, and with **23** added.

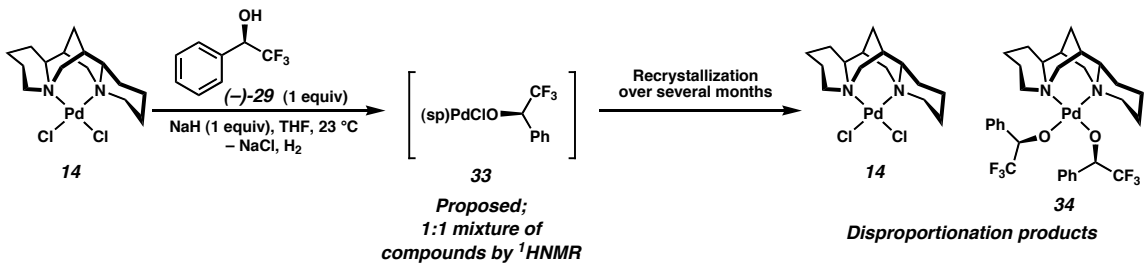




(sparteine)Pd(OCH(CF$_3$)C$_6$H$_5$)Cl (31). (+)-*S*-α-(trifluoromethyl)benzyl alcohol (**(+)-29**, 97 μL, 0.713 mmol, 1.0 equiv) was treated with an excess of sodium hydride (60% dispersion in mineral oil, 57 mg, 1.43 mmol, 2.0 equiv) in THF (5 mL) under argon. After bubbling had ceased, the alkoxide was transferred to a stirring suspension of (sparteine)PdCl$_2$ (**14**) (294 mg, 0.713 mmol, 1.0 equiv) in THF (19 mL) under argon at 23 °C. The yellow-orange suspension gradually became an orange solution with very fine white precipitate. After stirring for 30 min, the orange solution was filtered away from the sodium chloride and the solvents removed under vacuum to afford an orange solid (336 mg, 0.61 mmol, 84% yield) of 74% purity. **31** was obtained after recrystallization from CH_2Cl_2 layered with hexane at -20 °C in a glove box as an unstable dark orange solid (215 mg 0.39 mmol, 64% yield from crude material). The ^{1}H NMR spectrum of the crystalline material corresponded to that of the major species in the crude product. A single crystal suitable for X-ray diffraction was grown from CH_2Cl_2 layered with hexane at –20 °C. ^{1}H NMR (300 MHz, benzene-d_6) δ 7.40 (d, J = 7.8 Hz, 2H), 7.26-7.16 (comp. m, 3H), 4.92 (q, J_{HF} = 8.0 Hz, 1H), 4.34 (d, J = 11.3 Hz, 1H), 3.52-3.33 (comp. m, 3H), 2.66-2.54 (comp. m, 2H), 2.30-0.98 (comp. m, 20H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 129.9, 128.9, 128.8, 128.54, 128.47, 128.2, 78.5 (d, J = 27.7), 69.9, 65.7, 65.6, 64.3, 57.4, 49.2, 35.4, 34.9, 29.8, 28.0, 27.4, 25.3, 24.7, 24.2, 20.5; ^{19}F NMR (282 MHz, CD_2Cl_2) δ –76.2 (d, J_{FH} = 8.6 Hz).

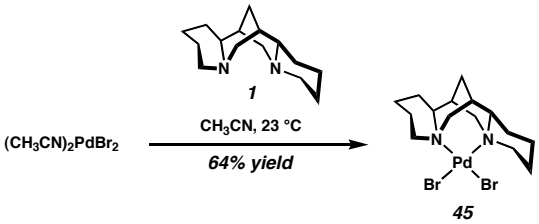


Conversion of 31 to 2,2,2-trifluoroacetophenone (32). **31** (18.8 mg, 0.034 mmol, 1.0 equiv) and bis(trimethylsilyl)benzene (4.4 mg, 0.021 mmol, 0.59 equiv) as internal standard were dissolved in CD_2Cl_2 (700 μL) in an NMR tube in the glove box. A ^{1}HNMR spectrum was acquired and the integration of resonances corresponding to the methine proton of **31** and the methyl resonance of bis(trimethylsilyl)benzene compared. The tube was taken into the glovebox, and $AgSbF_6$ (17.5 mg, 0.051 mmol, 1.5 equiv) was added to the orange solution upon which a greenish-black suspension was produced immediately. A ^{1}H NMR spectrum was acquired that showed complete disappearance of resonances corresponding to **31** and the appearance of resonances corresponding to 2,2,2-trifluoroacetophenone (**32**, 92% yield based on integration of the *ortho*-aryl ^{1}H resonance of 2,2,2-trifluoroacetophenone (**32**) and the methyl resonance of bis(trimethylsilyl)benzene and comparison with the first spectrum).



(sparteine)Pd(OCH(CF$_3$)C$_6$H$_5$)$_2$ (34). (–)-*R*-α-(trifluoromethyl)benzyl alcohol (**(–)-29**, 99 μL, 0.729 mmol, 1.0 equiv) was treated with 1 equiv of sodium hydride (60% dispersion in mineral oil, 58 mg, 1.46 mmol, 1.0 equiv) in THF (5 mL) under argon. After bubbling had ceased, the alkoxide was transferred to a stirring suspension of (sparteine)PdCl$_2$ (**14**) (300 mg, 0.729 mmol, 1.0 equiv) in THF (20 mL) under argon at 23 °C. The yellow-orange suspension gradually became an orange solution with very fine white precipitate. After stirring for 30 min, the orange solution was filtered away from the sodium chloride and the solvents removed under vacuum to afford an orange solid. A ^{1}H NMR spectrum of this material showed a 1:1 mixture of products. Recrystallization at –20 °C in a glove box from slow diffusion of hexane into a saturated solution of the material in CH_2Cl_2 after several months provided a mixture of yellow and orange crystals. The orange crystals were identified as **14** by X-ray crystallography and ^{1}H NMR. A solid-state structure of the unstable yellow crystals was obtained by X-ray crystallography at -20 °C identifiying **34**. The ^{1}H NMR spectrum of the crystalline material did not correspond that of the crude material. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.20-6.99 (comp. m, 10H), 4.53- 4.39 (comp. m, 3H), 3.84 (ddd, *J* = 12.2, 2.3, 2.3 Hz, 1H), 3.70-3.55 (comp. m, 2H), 3.41 (ddd, *J* = 16.7, 13.0, 3.8 Hz, 1H), 2.92 (dd, *J* = 13.0, 3.4 Hz, 1H), 2.79-2.70 (comp. m, 3H), 2.39 (dd, *J* = 12.5, 3.0 Hz, 1H), 2.06-1.25 (comp. m, 16H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 128.8, 128.7, 128.1, 127.8, 127.7, 127.7, 127.6, 78.3 (d, J_{CF} = 26.5 Hz), 77.5 (d, J_{CF} = 26.5 Hz), 70.2, 65.5, 65.4, 61.4, 58.0, 49.3, 35.6, 35.4, 30.6, 28.5, 27.2, 25.1, 24.8, 24.3, 20.4; ^{19}F NMR (282 MHz, CD_2Cl_2) δ –75.75 (d, J_{FH} = 9.2 Hz), –75.90 (d, J_{FH} = 9.2 Hz).

The preparation of (sp)PdBr$_2$ (45) and the reactions thereof.



(sp)PdBr$_2$ (45). $(CH_3CN)_2PdBr_2$[4] (250 mg, 0.72 mmol, 1 equiv) was suspended in CH_3CN (8 mL) under argon at 23 °C. (–)-Sparteine (**1**) was added, which quickly resulted in a dark red-orange solution. After 3 h stirring, a precipitate was visible. Et_2O (10 mL) was added, the mixture triturated, and filtered to provide **45** (230 mg, 0.46 mmol, 64% yield), as a purplish-orange powder. A single crystal suitable for X-ray analysis was grown by slow diffusion of hexane into a saturated CH_2Cl_2 solution of **45**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.53 (d, *J* = 11.6 Hz, 1H), 4.20-4.15 (m, 1H), 3.97 (br.d, *J* = 12.9 Hz, 1H), 3.52-3.39 (m, 1H), 3.24 (dd, *J* = 14.3, 1.4 Hz, 1H), 2.90-2.77 (comp. m, 2H), 2.45 (dd, *J* = 12.7, 3.0 Hz, 1H), 2.14-1.40 (comp. m, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 70.3, 67.6, 65.5, 64.9, 62.2, 49.1, 35.0, 34.8, 30.3, 28.0, 27.5, 26.0, 24.5, 23.8, 21.4; Anal. calc'd for $C_{15}H_{26}Br_2N_2Pd$: C, 35.99; H, 5.23; N, 5.60. Found: C, 35.62; H, 5.15; N, 5.53.

Oxidative kinetic resolution of 1-phenylethanol (28) with 45 shown in Table 3, Conditions "A," entry 1. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 100 mg, 500 mg/mmol), **45** (5.0 mg, 0.01 mmol, 0.05 equiv), and tridecane (15.0 μL, 0.062 mmol, 0.31 equiv) as internal standard, followed by toluene (2.0 mL), 1-phenylethanol (**28**), 24 μL, 0.20 mmol, 1 equiv), and (–)-sparteine (**1**) (3.3 mg, 0.014 mmol, 0.07 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon), heated to 60 °C, and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (200 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported.[1]

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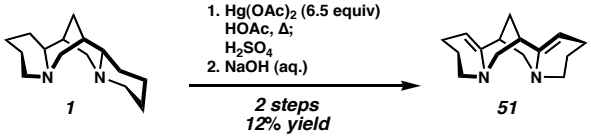
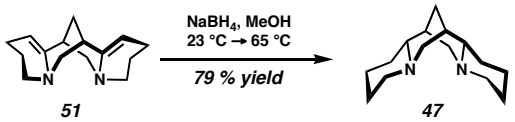
[4] Prepared by heating $PdBr_2$ in CH_3CN to reflux under nitrogen for 2 h.

Oxidative kinetic resolution of 1-phenylethanol (28) with 45 shown in Table 3 conditions "B," entry 2. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 100 mg, 500 mg/mmol), **45** (5.0 mg, 0.01 mmol, 0.05 equiv), anhydrous Cs_2CO_3 (26 mg, 0.08 mmol, 0.40 equiv) and tridecane (15.0 μL, 0.062 mmol, 0.31 equiv) as internal standard, followed by $CHCl_3$ (2.0 mL), 1-phenylethanol (**28**, 24 μL, 0.20 mmol, 1 equiv), and (–)-sparteine (**1**) (3.3 mg, 0.014 mmol, 0.07 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon) and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (200 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported.[1]



Didehydrosparteine (51). **51** was prepared according to the method of Leonard.[5] (–)-Sparteine **1**, 5.1 g, 21.0 mmol, 1 equiv) was dissolved in a 10% aqueous solution of AcOH (70 mL). This solution was added to a stirring suspension of $Hg(OAc)_2$ (43.4 g, 136 mmol, 6.5 equiv) in H_2O (60 mL). The mixture was heated to reflux under argon, during which time a pearlescent precipitate (HgOAc) formed. After 7 h, the mixture was allowed to cool to 23 °C. HgOAc was removed by filtration, and H_2S gas was bubbled through the yellow filtrate for 15 min to remove excess $Hg(OAc)_2$, during which time a fine black precipitate formed. Filtration of the mixture over Celite and a fine fritted funnel removed the black precipitate. The filtrate was acidified with aqueous H_2SO_4, and water was subsequently evaporated under vacuum. The resulting partially crystalline oily substance was triturated in methanol and filtered to provide the bisulfate salt as an off-white powder (3.18 g, 9.41 mmol, 45% yield). The salt (1.5 g, 4.45 mmol) was treated with 20% aqueous NaOH (50 mL) and extracted with Et_2O (5 x 25 mL). The solvent was removed under reduced pressure to provide a brown residue. The crude residue was sublimed at 90-100 °C at 20 millitorr to provide the free base (**51**) as a white powder (282 mg, 1.18 mmol, 26.5% yield). **51** was unstable to air at 23 °C, and was thus stored in the freezer under argon. The ^{1}H NMR spectrum was identical to that reported by Okamoto and Yuki.[6] ^{1}H NMR (500 MHz, benzene-d_6) δ 4.64 (br s, 2H), 3.09 (d, J = 9.3 Hz, 2H), 2.95 (dddd, J = 11.3, 4.9, 3.3, 2.0 Hz, 2H), 2.81 (dd, J = 10.1, 3.8 Hz, 2H), 2.66 (ddd, J = 11.0, 11.0, 2.8 Hz, 2H), 2.36-2.35 (m, 2H), 2.26 (dddd, J = 16.2, 10.0, 5.7, 2.1 Hz, 2H), 2.12-2.05 (comp. m, 2H), 2.01-1.92 (comp. m, 2H), 1.70-1.64 (comp. m, 4H); ^{13}C NMR (125 MHz, benzene-d_6) δ 147.0, 93.9, 60.4, 51.3, 37.4, 30.6, 23.1, 22.8; IR (film) 2927, 1643, 1358, 1315 cm^{-1}.



(–)-α-Isosparteine (47). Didehydrosparteine (**51**) was reduced according to the procedure of Okamoto and Yuki.[6] A mixture of didehydrosparteine (**51**, 300 mg, 1.25 mmol, 1 equiv) and $NaBH_4$ (1.90 g, 50.1 mmol, 40 equiv) in methanol (15 mL) was allowed to stir at 23 °C for 12 h. Additional methanol

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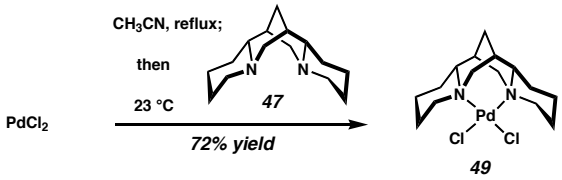
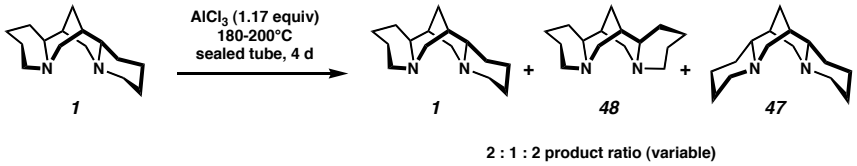
[5] Leonard, N. J.; Beyler, R. E. *J. Am. Chem. Soc.* **1950**, *72*, 1316-1323.

[6] Okamoto, Y.; Suzuki, K.; Kitayama, T.; Yuki, H.; Kageyama, H.; Miki, K.; Tanaka, N.; Kasai, N. *J. Am. Chem. Soc.* **1982**, *104*, 4618-4624.

(10 mL) was added, and the mixture heated to reflux for 1 h. After cooling to 23 °C, the crude reaction mixture was poured into ice water (15 mL) and basified with 20% aqueous NaOH. The solution was extracted with Et_2O (5 x 75 mL), dried over K_2CO_3, filtered, and concentrated in vacuo to give a white hygroscopic powder. The crude product was sublimed at 65-70 °C at 20 millitorr. The sublimation apparatus was brought into a nitrogen atmosphere glovebox, and **47** collected (239 mg, 0.982 mmol, 79% yield). The ^{1}H NMR spectrum was identical to that reported by Okamoto and Yuki.[6] ^{1}H NMR (500 MHz, benzene-d_6) δ 2.99 (d, J = 11.2 Hz, 2H), 2.78-2.74 (m, 2H), 2.08 (dd, J = 11.1, 2.9 Hz, 2H), 1.89 (br. d, J = 10.9 Hz, 2H), 1.82-1.64 (comp. m, 8H), 1.55-1.54 (m, 2H), 1.42-1.20 (comp. m, 8H); ^{13}C NMR (125 MHz, benzene-d_6) δ 66.6, 58.0, 57.3, 37.3, 36.7, 31.3, 26.6, 26.1; IR (film) 2930, 1444, 1287, 1106 cm^{-1}.



(α-isosparteine)PdCl$_2$ 49. $(CH_3CN)_2PdCl_2$ (73 mg, 0.28 mmol, 1.0 equiv) and (–)-α-isosparteine (**47**, 66 mg, 0.28 mmol, 1.0 equiv) were dissolved in CH_3CN (5 mL) and allowed to stir at 23 °C under argon for 1 h. The dark orange solution was filtered through Celite and concentrated in vacuo to afford **49** as a rust-colored crystalline solid (84 mg, 0.20 mmol, 72% yield). A single crystal suitable for X-ray diffraction was grown by slow evaporation from CH_2Cl_2. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 3.95 (dddd, J = 12.4, 12.4, 12.4, 3.9 Hz, 2H), 3.72-3.66 (m, 2H), 3.51 (d, J = 12.4 Hz, 2H), 2.98-2.84 (m, 2H), 2.24-2.19 (m, 2H), 2.15-2.10 (m, 2H) 1.94-1.79 (comp. m, 10 H), 1.65-1.51 (comp. m, 4 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 72.15, 64.6, 60.7, 35.8, 35.5, 30.9, 25.5, 25.0. Anal. calc'd for $C_{15}H_{26}Cl_2N_2Pd$: C, 43.76; H, 6.37; N, 6.80. Found: C, 43.82; H, 6.36; N, 6.68; mp 180-182 °C.



(+)-β-Isosparteine (48). **48** was prepared by the method of Winterfeld.[7] Freshly sublimed $AlCl_3$ (2.41 g, 18.1 mmol, 1.17 equiv) was transferred to a Schlenk flask in the glovebox. The flask was taken out of the box and distilled (–)-sparteine (**1**) (3.96 g, 16.9 mmol, 1 equiv) added under a stream of argon, upon which a small amount of vapor and heat was produced. The flask was sealed and heated to 180-200 °C in a sand bath behind a blast shield. Additional vapor was produced which dissipated after ca. 15 min. The product mixture formed a bright red melt of low viscosity at high temperatures. After 4 d, the flask was cooled to 23 °C upon which the red liquid solidified into a hard glass. The solid was scraped out of the flask with the assistance of 3 M HCl (50 mL) which produced a yellow solution. This solution was basified with KOH and extracted with Et_2O (6 x 50 mL). The organic extracts were dried over K_2CO_3, filtered, and concentrated in vacuo to provide ca. 4.3 g of a 2:1:2 mixture of **1**, (+)-β-isosparteine (**48**), and (–)-α-isosparteine (**47**). The mixture was purified by repeated column chromatography on SiO_2 with mixtures of CH_2Cl_2, methanol and NH_4OH as eluent. A 100:10:1 mixture was gradually ramped up to a 85:15:1.5 eluent mixture, then to 75:25:2.5 and lastly 60:40:4 CH_2Cl_2:MeOH:NH_4OH. (–)-Sparteine (**1**) elutes first, followed quickly by (+)-β-isosparteine (**48**), and, much later, (–)-α-isosparteine (**47**), which is isolated as its hydrate. TLC analysis by iodoplatinate staining was of some assistance in tracking column progress. Repeated column chromatography of partially separated diastereomers (mostly **1** and **48**) yields approximately 500 mg of pure (+)-β-isosparteine (**48**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94 (dd, J = 10.7, 6.3 Hz, 2H), 2.77 (dddd, J = 12.4, 4.1, 2.1, 1.9 Hz, 2H), 2.45 (ddd, J = 12.4, 12.4, 2.8 Hz, 2H), 2.31 (ddd, J

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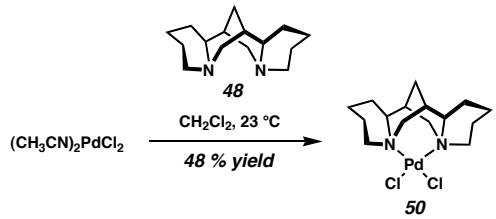
[7] Winterfeld, K.; Bange, H.; Lalvani, K. S. *Justus Liebigs Ann. Chem.* **1966**, *698*, 230-234.

= 11.8, 2.5, 2.5 Hz, 2H), 2.22 (dd, *J* = 10.7, 2.8 Hz, 2H), 1.72-1.49 (comp. m, 10H), 1.36-1.10 (comp. m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 63.3, 55.9, 55.7, 35.6, 29.4, 26.4, 23.6, 20.6; IR (film) 2925, 1447, 1357, 1129 cm^{-1}; $[\alpha]_D^{21.1}$ +15.38 (*c* 0.142, absolute EtOH).



((+)-β-isosparteine)$PdCl_2$ (50). (+)-β-Isosparteine (**48**, 48 mg, 0.21 mmol, 1 equiv) was taken up in CH_2Cl_2 (4 mL) under argon. The flask was opened and $(CH_3CN)_2PdCl_2$ (53 mg, 0.21 mmol, 1 equiv) was added quickly as a solid. The resulting dark red-orange solution was allowed to stir at 23 °C for 16 h. After the solution was filtered through glass filter paper to remove a small amount of palladium black, the solvents were evaporated to give an orange powder. Trituration with pentane from CH_2Cl_2 provided **50** (41 mg, 0.10 mmol, 48% yield) as a light orange powder. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 3.85-3.75 (comp. m, 4H), 3.26-3.03 (comp. m, 6H), 1.99-1.33 (comp. m, 16H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 64.8, 64.5, 56.0, 35.2, 28.0, 23.9, 21.4, 20.5; Anal. calc'd for $C_{15}H_{26}Cl_2N_2Pd$: C, 43.76; H, 6.37; N, 6.80. Found: C, 43.97; H, 6.41; N, 6.81.

Oxidative kinetic resolution of 1-phenylethanol (28) with 49, 50 or 14 shown in Table 4, representative procedure. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 150 mg, 500 mg/mmol), **49**, **50** or **14** (6.2 mg, 0.015 mmol, 0.05 equiv), and tridecane (29.3 μL, 0.12 mmol, 0.40 equiv) as internal standard, followed by toluene (3.0 mL), 1-phenylethanol (**28**, 36 μL, 0.30 mmol, 1 equiv), and (–)-α-isosparteine (**47**), (+)-β-isosparteine (**48**), or (–)-sparteine (**12**, 10.5 mg, 0.045 mmol, 0.15 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon), heated to 80 °C, and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (200 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported.[1]

Oxidative kinetic resolution of 1-phenylethanol (28) with 49, 50 and 14 with Cs_2CO_3 as the sole exogenous base shown in Table 4, representative procedure. A thick-walled oven-dried 10 mL (1 cm OD) tube equipped with magnetic stir bar was charged with powdered molecular sieves (MS3Å, 150 mg, 500 mg/mmol), 49, 50 or 14 (6.2 mg, 0.015 mmol, 0.05 equiv), and tridecane (29.3 μL, 0.12 mmol, 0.40 equiv) as internal standard, followed by toluene (3.0 mL), 1-phenylethanol (28, 36 μL, 0.30 mmol, 1 equiv), and finely ground anhydrous Cs_2CO_3 (98 mg, 0.300 mmol, 1 equiv). The tube was evacuated and back-filled with O_2 (3 x, balloon), heated to 80 °C, and allowed to stir under O_2 (1 atm, balloon). To monitor the reaction, aliquots (100 μL) were removed and passed through a pipette plug of silica gel using Et_2O as eluent. Conversion was analyzed by GC; the sample was then concentrated in vacuo and %ee analyzed by chiral HPLC as previously reported.[8]

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[8] (a) Bagdanoff, J. T.; Ferreira, E. M.; Stoltz, B. M. *Org. Lett.* **2003**, *5*, 835-837. (b) Bagdanoff, J. T.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 353-357.

X-ray crystallographic structures.

We have reported the x-ray crystallographic structure for (sparteine)$PdCl_2$ (**14**) elsewhere.[1,9]

X-ray crystallographic structure for **[(sparteine)Pd(pyridine)Cl]$^+$SbF$_6^-$ (16)**. The crystallographic data for **16** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 213927.

Crystal data and structural refinement for 16 (CCDC 213927).

Empirical formula	$[C_{20}H_{31}ClN_3Pd]^+$ $[SbF_6]^-$
Formula weight	691.08
Crystallization Solvent	Acetone/pentane
Crystal Habit	Block
Crystal size	0.23 x 0.20 x 0.19 mm^3
Crystal color	Yellow
Data Collection	
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection	
Temperature	100(2) K
θ range for 54240 reflections used in lattice determination	2.19 to 39.64°
Unit cell dimensions	a = 10.3598(2) Å b = 22.2422(3) Å β= 104.3020(10)° c = 10.8117(2) Å
Volume	2414.07(7) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.901 Mg/m^3
F(000)	1360
Data collection program	Bruker SMART v5.054
θ range for data collection	1.83 to 40.92°
Completeness to θ = 40.92°	97.6 %
Index ranges	$-18 \le h \le 18$, $-40 \le k \le 40$, $-19 \le l \le 19$
Data collection scan type	ω scans at 7 ϕ and 2 2θ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	110239
Independent reflections	29947 [R_{int}= 0.0717]
Absorption coefficient	2.034 mm^{-1}
Absorption correction	Calculated, **NOT** applied
Max. and min. transmission	0.6986 and 0.6520
Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2

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[9] Trend, R. M.; Stoltz, B.M. *J. Am. Chem. Soc.* **2004**, *126*, 4482-4483.

Data / restraints / parameters	29947 / 1 / 577
Treatment of hydrogen atoms	Constrained
Goodness-of-fit on F^2	1.664
Final R indices [I>2σ(I), 22793 reflections]	R1 = 0.0503, *w*R2 = 0.0842
R indices (all data)	R1 = 0.0709, *w*R2 = 0.0864
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.018(12)
Largest diff. peak and hole	5.743 and -4.948 e.Å^{-3}

Special refinement details

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

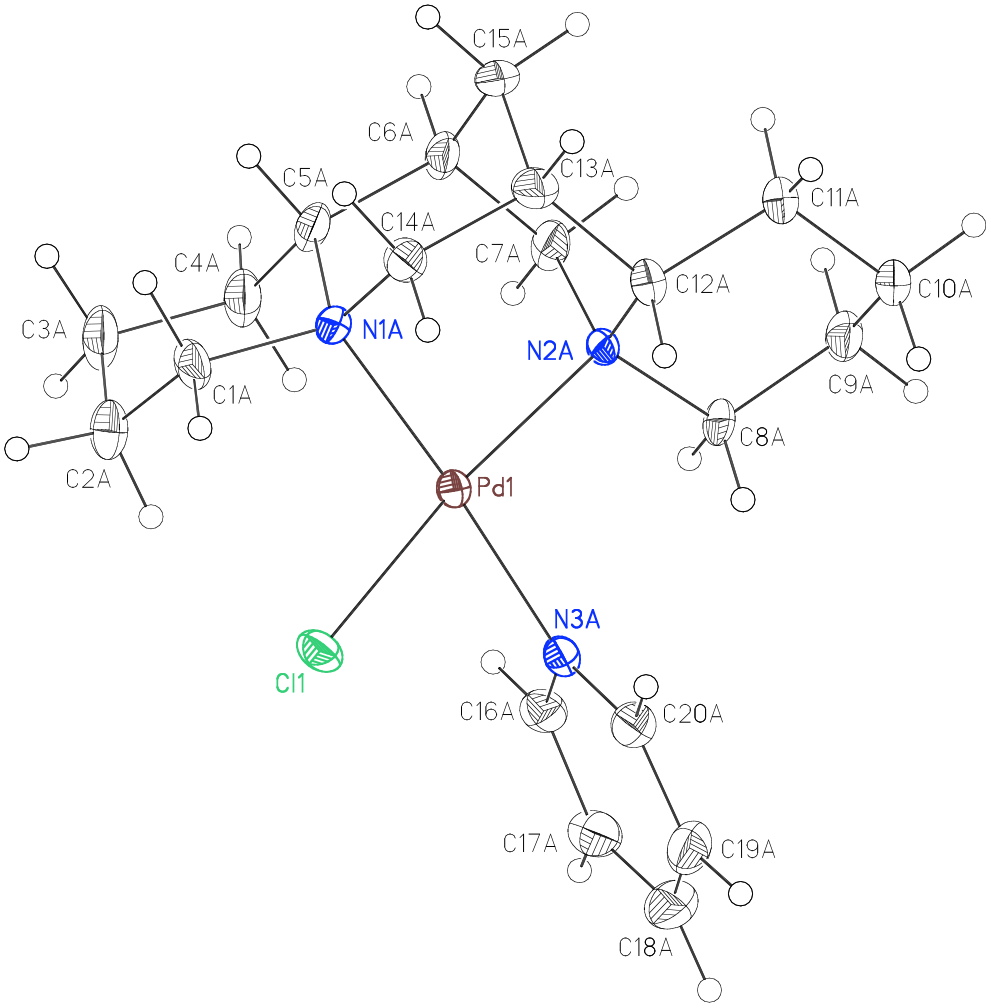

Figure S2. Molecule A of **16**. The SbF_6 anion is not shown.

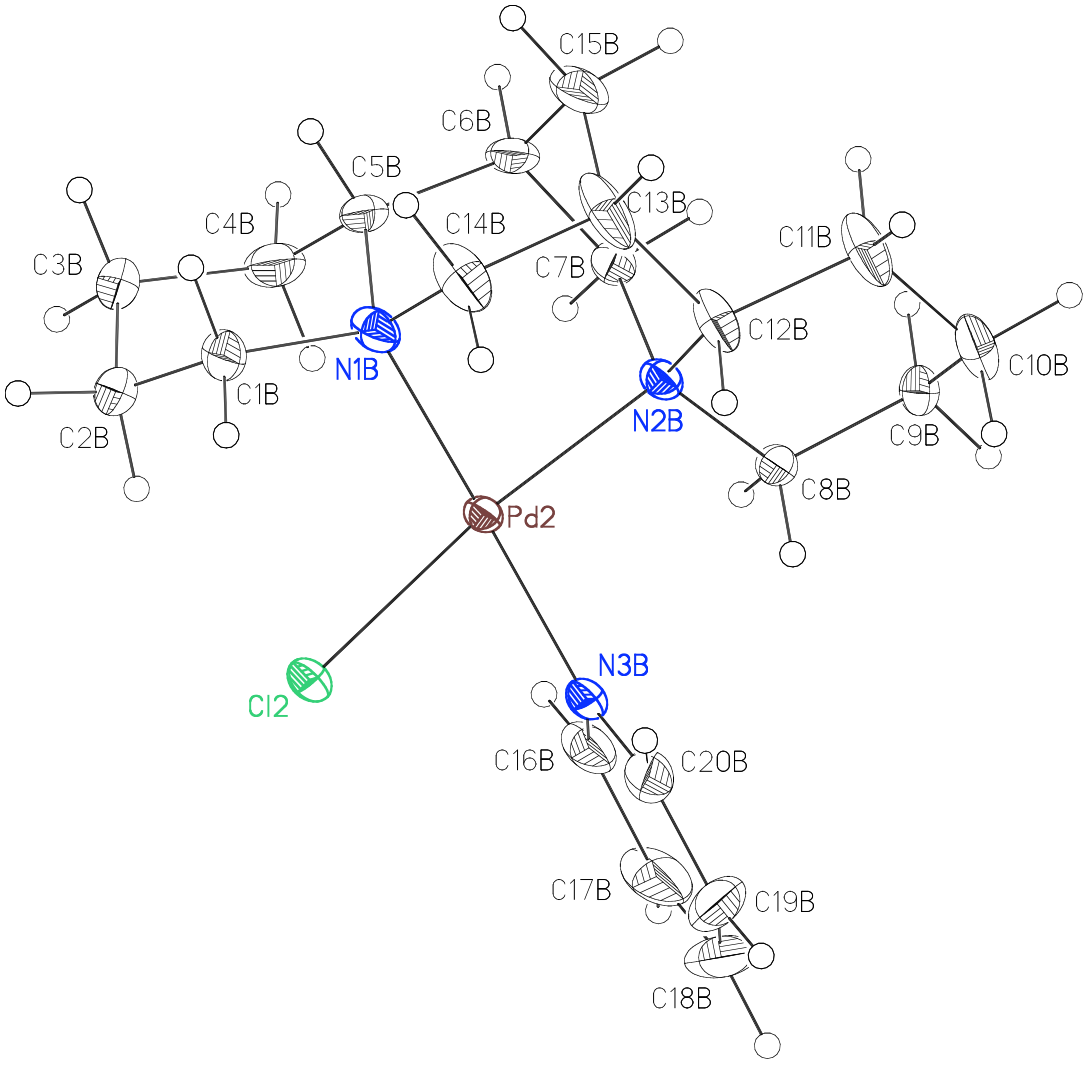

Figure S3. Molecule B of **16**. The SbF_6 anion is not shown.

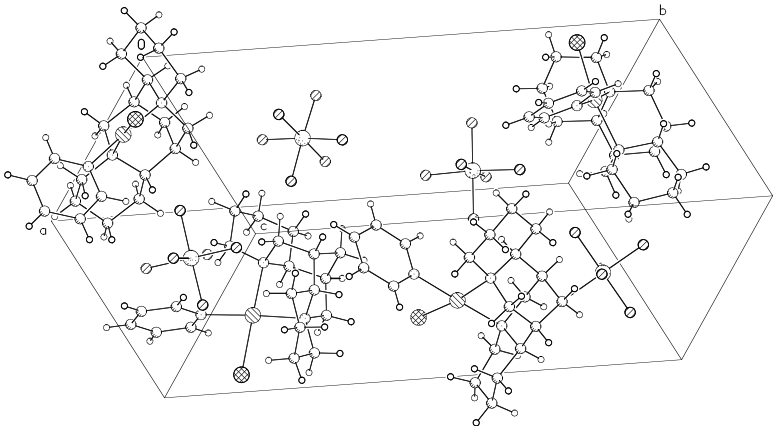

Figure S4. Unit cell contents of **16**.

Table S1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **16** (CCDC 213927). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	10320(1)	2723(1)	5621(1)	14(1)
Cl(1)	12080(1)	2448(1)	7292(1)	22(1)
N(1A)	9566(2)	3377(1)	6637(2)	18(1)
N(2A)	9001(2)	3065(1)	3945(2)	15(1)
N(3A)	11093(2)	2054(1)	4722(2)	17(1)
C(1A)	10112(3)	3338(2)	8078(3)	23(1)
C(2A)	9698(3)	2751(2)	8630(3)	26(1)
C(3A)	8180(3)	2674(2)	8277(3)	31(1)
C(4A)	7680(3)	2736(2)	6840(3)	27(1)
C(5A)	8067(3)	3341(2)	6411(3)	23(1)
C(6A)	7375(3)	3512(2)	5054(3)	26(1)
C(7A)	7584(3)	3077(2)	4038(3)	24(1)
C(8A)	9095(3)	2672(2)	2831(2)	20(1)
C(9A)	8413(3)	2933(2)	1536(3)	26(1)
C(10A)	9048(4)	3532(2)	1363(3)	26(1)
C(11A)	8921(4)	3954(2)	2440(3)	28(1)
C(12A)	9527(3)	3683(2)	3778(3)	22(1)
C(13A)	9256(3)	4118(2)	4823(3)	24(1)
C(14A)	9992(3)	3962(2)	6193(3)	22(1)
C(15A)	7760(4)	4151(2)	4766(3)	30(1)
C(16A)	10559(3)	1497(2)	4646(3)	22(1)
C(17A)	11158(3)	1014(2)	4253(3)	28(1)
C(18A)	12354(4)	1099(2)	3895(3)	34(1)
C(19A)	12886(3)	1669(2)	3974(3)	29(1)
C(20A)	12237(3)	2131(2)	4392(3)	22(1)
Pd(2)	3905(1)	147(1)	783(1)	13(1)
Cl(2)	2076(1)	-111(1)	1564(1)	21(1)
N(1B)	3125(2)	946(1)	-112(3)	22(1)
N(2B)	5730(2)	363(1)	299(2)	17(1)
N(3B)	4640(3)	-612(1)	1749(3)	24(1)
C(1B)	1684(3)	1064(2)	-122(3)	26(1)
C(2B)	696(3)	661(2)	-1013(3)	27(1)
C(3B)	907(3)	650(2)	-2361(4)	33(1)
C(4B)	2384(4)	514(2)	-2287(4)	32(1)
C(5B)	3216(3)	991(2)	-1490(3)	32(1)
C(6B)	4667(3)	1007(2)	-1585(4)	31(1)
C(7B)	5481(3)	459(2)	-1104(3)	22(1)
C(8B)	6705(3)	-140(1)	674(3)	20(1)
C(9B)	8115(3)	-3(2)	620(3)	22(1)
C(10B)	8636(3)	520(2)	1497(3)	30(1)
C(11B)	7722(3)	1059(2)	1087(4)	33(1)
C(12B)	6250(3)	920(2)	1058(3)	25(1)
C(13B)	5362(3)	1466(2)	515(5)	39(1)
C(14B)	3935(3)	1423(2)	675(4)	34(1)
C(15B)	5302(4)	1558(2)	-890(5)	44(1)
C(16B)	4655(4)	-1135(2)	1170(5)	35(1)
C(17B)	5123(4)	-1642(2)	1878(6)	62(2)
C(18B)	5569(5)	-1610(3)	3196(7)	87(3)
C(19B)	5540(4)	-1057(3)	3785(5)	63(2)
C(20B)	5068(3)	-567(2)	3054(4)	38(1)
Sb(1)	6705(1)	950(1)	5357(1)	40(1)
F(1A)	5882(5)	325(2)	5990(4)	102(2)
F(2A)	7934(4)	1054(3)	6895(4)	136(2)
F(3A)	7451(4)	1562(2)	4591(4)	84(1)
F(4A)	5439(2)	852(2)	3818(2)	61(1)

F(5A)	5618(2)	1517(1)	5894(2)	48(1)
F(6A)	7826(3)	406(2)	4785(3)	65(1)
Sb(2)	3555(1)	3287(1)	1991(1)	27(1)
F(1B)	2277(2)	2665(1)	1700(2)	48(1)
F(2B)	4500(3)	2908(2)	3474(3)	98(2)
F(3B)	4846(2)	3897(1)	2246(3)	52(1)
F(4B)	2567(3)	3679(1)	579(3)	69(1)
F(5B)	4555(3)	2890(2)	1067(4)	83(1)
F(6B)	2601(3)	3656(2)	3051(4)	98(2)

Table S2. Bond lengths [Å] and angles [°] for **16** (CCDC 213927).

Pd(1)-N(3A)	2.046(3)	C(3B)-C(4B)	1.543(5)
Pd(1)-N(1A)	2.087(2)	C(4B)-C(5B)	1.498(6)
Pd(1)-N(2A)	2.122(2)	C(5B)-C(6B)	1.532(4)
Pd(1)-Cl(1)	2.3105(7)	C(6B)-C(15B)	1.501(6)
N(1A)-C(14A)	1.492(4)	C(6B)-C(7B)	1.501(5)
N(1A)-C(5A)	1.513(4)	C(8B)-C(9B)	1.507(4)
N(1A)-C(1A)	1.523(3)	C(9B)-C(10B)	1.514(5)
N(2A)-C(7A)	1.496(4)	C(10B)-C(11B)	1.523(5)
N(2A)-C(12A)	1.507(4)	C(11B)-C(12B)	1.548(4)
N(2A)-C(8A)	1.510(4)	C(12B)-C(13B)	1.549(5)
N(3A)-C(20A)	1.331(4)	C(13B)-C(15B)	1.519(7)
N(3A)-C(16A)	1.351(4)	C(13B)-C(14B)	1.533(5)
C(1A)-C(2A)	1.539(5)	C(16B)-C(17B)	1.381(6)
C(2A)-C(3A)	1.534(5)	C(17B)-C(18B)	1.388(9)
C(3A)-C(4A)	1.518(4)	C(18B)-C(19B)	1.390(10)
C(4A)-C(5A)	1.510(5)	C(19B)-C(20B)	1.363(6)
C(5A)-C(6A)	1.514(4)	Sb(1)-F(2A)	1.842(3)
C(6A)-C(7A)	1.518(4)	Sb(1)-F(1A)	1.848(4)
C(6A)-C(15A)	1.530(5)	Sb(1)-F(3A)	1.858(3)
C(8A)-C(9A)	1.521(4)	Sb(1)-F(4A)	1.860(2)
C(9A)-C(10A)	1.517(5)	Sb(1)-F(5A)	1.876(3)
C(10A)-C(11A)	1.526(5)	Sb(1)-F(6A)	1.883(3)
C(11A)-C(12A)	1.550(4)	Sb(2)-F(5B)	1.834(3)
C(12A)-C(13A)	1.563(4)	Sb(2)-F(4B)	1.835(2)
C(13A)-C(14A)	1.529(4)	Sb(2)-F(2B)	1.861(3)
C(13A)-C(15A)	1.537(5)	Sb(2)-F(6B)	1.878(3)
C(16A)-C(17A)	1.360(5)	Sb(2)-F(3B)	1.879(3)
C(17A)-C(18A)	1.399(5)	Sb(2)-F(1B)	1.886(2)
C(18A)-C(19A)	1.376(6)	N(3A)-Pd(1)-N(1A)	176.64(10)
C(19A)-C(20A)	1.365(5)	N(3A)-Pd(1)-N(2A)	95.73(9)
Pd(2)-N(3B)	2.031(3)	N(1A)-Pd(1)-N(2A)	87.39(9)
Pd(2)-N(1B)	2.087(3)	N(3A)-Pd(1)-Cl(1)	81.52(7)
Pd(2)-N(2B)	2.136(2)	N(1A)-Pd(1)-Cl(1)	95.67(7)
Pd(2)-Cl(2)	2.3294(7)	N(2A)-Pd(1)-Cl(1)	168.52(7)
N(1B)-C(14B)	1.484(4)	C(14A)-N(1A)-C(5A)	111.5(2)
N(1B)-C(1B)	1.514(4)	C(14A)-N(1A)-C(1A)	108.3(2)
N(1B)-C(5B)	1.519(4)	C(5A)-N(1A)-C(1A)	105.6(2)
N(2B)-C(7B)	1.491(4)	C(14A)-N(1A)-Pd(1)	105.07(18)
N(2B)-C(8B)	1.494(4)	C(5A)-N(1A)-Pd(1)	112.38(19)
N(2B)-C(12B)	1.511(4)	C(1A)-N(1A)-Pd(1)	113.98(19)
N(3B)-C(16B)	1.324(5)	C(7A)-N(2A)-C(12A)	112.3(3)
N(3B)-C(20B)	1.374(5)	C(7A)-N(2A)-C(8A)	108.8(2)
C(1B)-C(2B)	1.513(5)	C(12A)-N(2A)-C(8A)	109.7(2)
C(2B)-C(3B)	1.526(5)	C(7A)-N(2A)-Pd(1)	112.62(18)

C(12A)-N(2A)-Pd(1)	104.67(17)
C(8A)-N(2A)-Pd(1)	108.57(17)
C(20A)-N(3A)-C(16A)	118.7(3)
C(20A)-N(3A)-Pd(1)	120.9(2)
C(16A)-N(3A)-Pd(1)	119.5(2)
N(1A)-C(1A)-C(2A)	112.1(3)
C(3A)-C(2A)-C(1A)	111.4(3)
C(4A)-C(3A)-C(2A)	108.3(3)
C(5A)-C(4A)-C(3A)	110.3(3)
C(4A)-C(5A)-N(1A)	109.7(3)
C(4A)-C(5A)-C(6A)	115.1(3)
N(1A)-C(5A)-C(6A)	111.4(2)
C(5A)-C(6A)-C(7A)	115.0(3)
C(5A)-C(6A)-C(15A)	110.3(3)
C(7A)-C(6A)-C(15A)	110.7(3)
N(2A)-C(7A)-C(6A)	112.2(3)
N(2A)-C(8A)-C(9A)	113.9(3)
C(10A)-C(9A)-C(8A)	109.4(3)
C(9A)-C(10A)-C(11A)	108.9(3)
C(10A)-C(11A)-C(12A)	112.5(3)
N(2A)-C(12A)-C(11A)	113.0(3)
N(2A)-C(12A)-C(13A)	110.1(2)
C(11A)-C(12A)-C(13A)	109.3(3)
C(14A)-C(13A)-C(15A)	107.8(3)
C(14A)-C(13A)-C(12A)	115.1(3)
C(15A)-C(13A)-C(12A)	111.1(3)
N(1A)-C(14A)-C(13A)	113.1(3)
C(6A)-C(15A)-C(13A)	104.9(3)
N(3A)-C(16A)-C(17A)	122.1(3)
C(16A)-C(17A)-C(18A)	119.0(3)
C(19A)-C(18A)-C(17A)	118.3(3)
C(20A)-C(19A)-C(18A)	119.5(3)
N(3A)-C(20A)-C(19A)	122.4(3)
N(3B)-Pd(2)-N(1B)	176.62(12)
N(3B)-Pd(2)-N(2B)	94.05(10)
N(1B)-Pd(2)-N(2B)	87.73(10)
N(3B)-Pd(2)-Cl(2)	80.99(7)
N(1B)-Pd(2)-Cl(2)	96.98(7)
N(2B)-Pd(2)-Cl(2)	172.89(7)
C(14B)-N(1B)-C(1B)	107.3(3)
C(14B)-N(1B)-C(5B)	110.6(3)
C(1B)-N(1B)-C(5B)	106.4(3)
C(14B)-N(1B)-Pd(2)	104.1(2)
C(1B)-N(1B)-Pd(2)	114.8(2)
C(5B)-N(1B)-Pd(2)	113.6(2)
C(7B)-N(2B)-C(8B)	108.6(2)
C(7B)-N(2B)-C(12B)	112.6(3)
C(8B)-N(2B)-C(12B)	109.9(2)
C(7B)-N(2B)-Pd(2)	109.87(18)
C(8B)-N(2B)-Pd(2)	110.24(18)
C(12B)-N(2B)-Pd(2)	105.69(17)
C(16B)-N(3B)-C(20B)	120.6(4)
C(16B)-N(3B)-Pd(2)	122.3(3)
C(20B)-N(3B)-Pd(2)	117.0(3)
C(2B)-C(1B)-N(1B)	114.4(3)
C(1B)-C(2B)-C(3B)	112.6(3)
C(2B)-C(3B)-C(4B)	109.1(3)
C(5B)-C(4B)-C(3B)	108.2(3)
C(4B)-C(5B)-N(1B)	110.6(3)
C(4B)-C(5B)-C(6B)	114.4(3)
N(1B)-C(5B)-C(6B)	111.6(3)
C(15B)-C(6B)-C(7B)	110.5(3)
C(15B)-C(6B)-C(5B)	107.6(3)
C(7B)-C(6B)-C(5B)	115.7(3)
N(2B)-C(7B)-C(6B)	114.2(3)
N(2B)-C(8B)-C(9B)	115.9(3)
C(8B)-C(9B)-C(10B)	109.2(3)
C(9B)-C(10B)-C(11B)	108.8(3)
C(10B)-C(11B)-C(12B)	112.8(3)
N(2B)-C(12B)-C(11B)	113.0(3)
N(2B)-C(12B)-C(13B)	109.8(3)
C(11B)-C(12B)-C(13B)	110.0(3)
C(15B)-C(13B)-C(14B)	108.6(4)
C(15B)-C(13B)-C(12B)	110.9(3)
C(14B)-C(13B)-C(12B)	114.0(3)
N(1B)-C(14B)-C(13B)	113.8(3)
C(6B)-C(15B)-C(13B)	107.2(3)
N(3B)-C(16B)-C(17B)	120.0(5)
C(16B)-C(17B)-C(18B)	120.7(5)
C(17B)-C(18B)-C(19B)	118.4(4)
C(20B)-C(19B)-C(18B)	119.1(5)
C(19B)-C(20B)-N(3B)	121.1(5)
F(2A)-Sb(1)-F(1A)	92.3(3)
F(2A)-Sb(1)-F(3A)	92.3(2)
F(1A)-Sb(1)-F(3A)	175.40(19)
F(2A)-Sb(1)-F(4A)	178.85(15)
F(1A)-Sb(1)-F(4A)	87.42(18)
F(3A)-Sb(1)-F(4A)	88.07(17)
F(2A)-Sb(1)-F(5A)	88.28(14)
F(1A)-Sb(1)-F(5A)	91.38(15)
F(3A)-Sb(1)-F(5A)	89.58(13)
F(4A)-Sb(1)-F(5A)	90.62(11)
F(2A)-Sb(1)-F(6A)	91.87(15)
F(1A)-Sb(1)-F(6A)	90.95(17)
F(3A)-Sb(1)-F(6A)	88.09(14)
F(4A)-Sb(1)-F(6A)	89.24(13)
F(5A)-Sb(1)-F(6A)	177.66(15)
F(5B)-Sb(2)-F(4B)	92.88(19)
F(5B)-Sb(2)-F(2B)	90.2(2)
F(4B)-Sb(2)-F(2B)	176.9(2)
F(5B)-Sb(2)-F(6B)	175.4(2)
F(4B)-Sb(2)-F(6B)	91.73(19)
F(2B)-Sb(2)-F(6B)	85.2(2)
F(5B)-Sb(2)-F(3B)	87.13(13)
F(4B)-Sb(2)-F(3B)	90.50(11)
F(2B)-Sb(2)-F(3B)	89.79(13)
F(6B)-Sb(2)-F(3B)	93.28(15)
F(5B)-Sb(2)-F(1B)	91.39(13)
F(4B)-Sb(2)-F(1B)	89.18(11)
F(2B)-Sb(2)-F(1B)	90.60(12)
F(6B)-Sb(2)-F(1B)	88.23(15)
F(3B)-Sb(2)-F(1B)	178.47(13)

X-ray crystallographic structure for **[(sparteine)Pd(2-methylisoquinoline)Cl]$^+$SbF$_6^-$ (19/20)**. The crystallographic data for **19/20** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 217276.

Crystal data and structural refinement for 19/20 (CCDC 217276)

Empirical formula	$[C_{25}H_{35}N_3ClPd]^+ [SbF_6]^-$
Formula weight	755.16
Crystallization Solvent	Dichloromethane
Crystal Habit	Block
Crystal size	0.30 x 0.28 x 0.27 mm^3
Crystal color	Orange

Data collection

Preliminary photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 29306 reflections used in lattice determination	2.25 to 28.19°
Unit cell dimensions	a = 9.7500(5) Å b = 21.3471(10) Å β = 91.4260(10)° c = 13.1934(6) Å
Volume	2745.1(2) Å^3
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.827 Mg/m^3
F(000)	1496
θ range for data collection	1.54 to 28.41°
Completeness to θ = 28.41°	93.1 %
Index ranges	$-12 \le h \le 12$, $-28 \le k \le 27$, $-17 \le l \le 17$
Data collection scan type	ω scans at 4 ϕ settings and 1 ϕ scan
Reflections collected	47919
Independent reflections	12521 [R_{int}= 0.0494]
Absorption coefficient	1.797 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.6425 and 0.6146

Structure solution and refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Patterson method
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	12521 / 1 / 542
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.140
Final R indices [I>2σ(I), 11419 reflections]	R1 = 0.0440, *w*R2 = 0.0763
R indices (all data)	R1 = 0.0505, *w*R2 = 0.0772
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure parameter	-0.028(18)
Largest diff. peak and hole	2.187 and -1.798 e.Å^{-3}

Special refinement details.

Disorder is observed in the crystals. One of the two molecules in the asymmetric unit is disordered in that both isomers with respect to the orientation of the isoquinoline ligand occupy the site. Molecule A has two orientations of the isoquinoline related by a rotation of 180° around the Pd-N bond. The atoms of both orientations were refined isotropically with riding hydrogen atoms. The occupancies of both orientations are nearly equal, see Table S3. The final difference Fourier map suggests similar disorder in the isoquinoline ligand of Molecule B but to a much lesser extent. Because the evidence was so weak no attempt was made to model it, anisotropic displacement parameters were used for nonhydrogen atoms. The isoquinoline ligands were refined with the ring systems set as rigid bodies (distances = 1.39Å). No restraints were placed on the methyl group.

The largest peak in the final difference Fourier map is within 0.8Å of Sb(2). All other peaks greater than 1.0e^-/Å^3 (four of them ranging from 1.41-1.06 e^-/Å^3) evidence unmodeled disorder.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

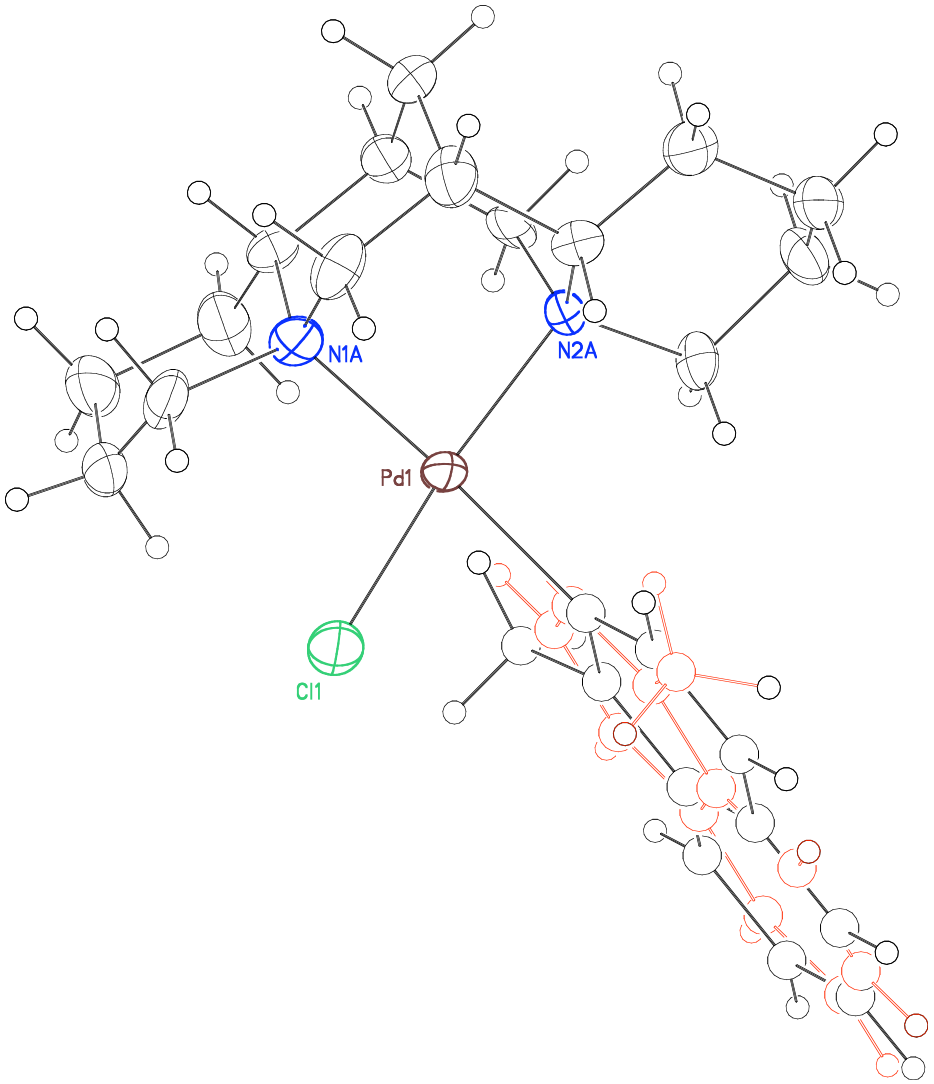

Figure S5. Molecule A of **19/20** showing the disorder in the isoquinoline ligand. The SbF_6 anion is not shown. The numbering differs from that shown in Scheme 4.

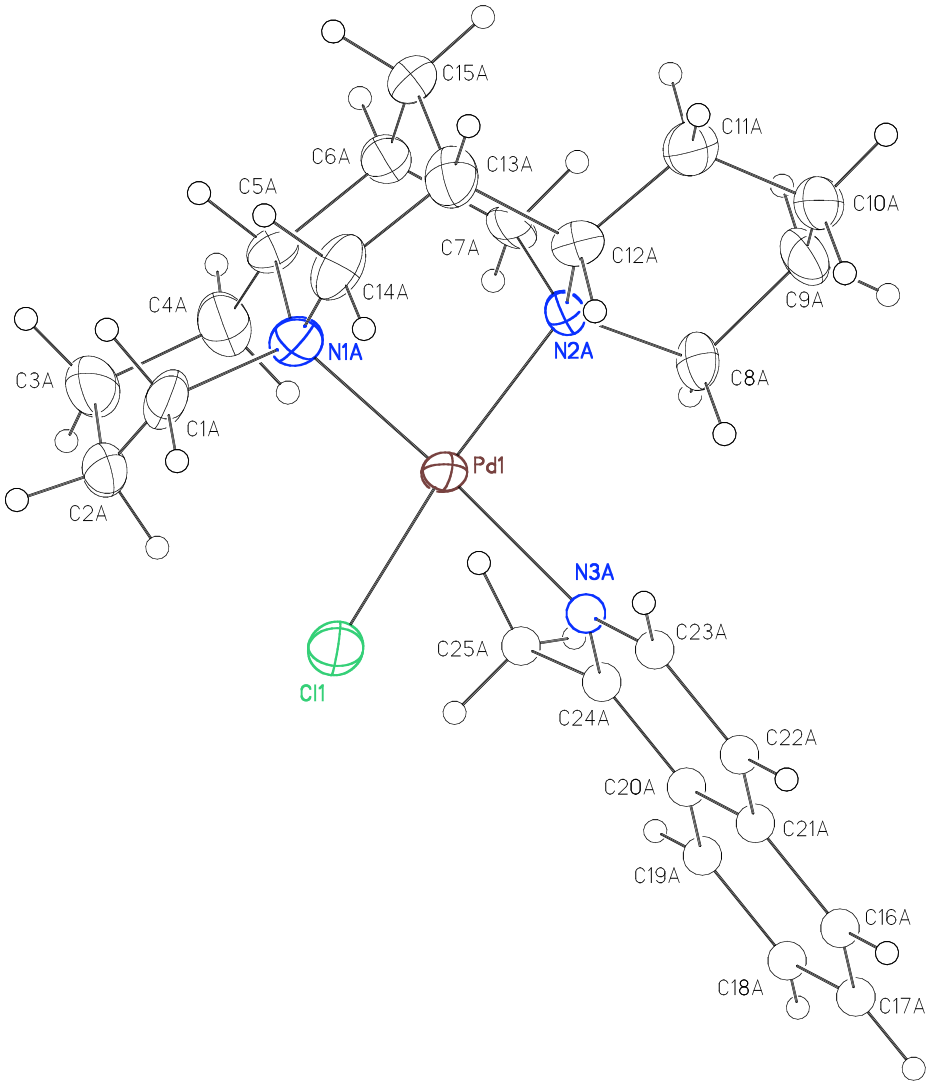

Figure S6. Molecule A of **19/20** showing the disorder modeled isotropically in one orientation of the isoquinoline ligand, i.e., **19**. The SbF_6 anion is not shown. The numbering differs from that shown in Scheme 4.

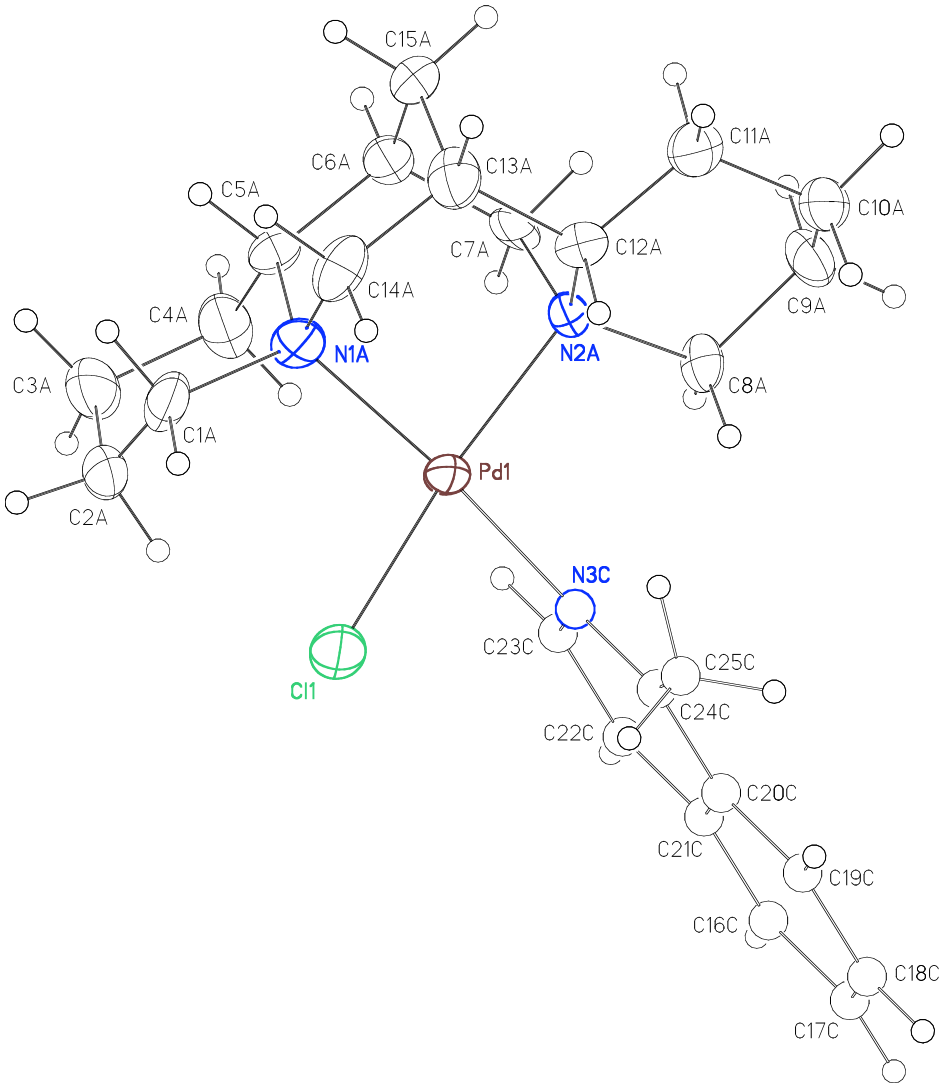

Figure S7. Molecule A of **19/20** showing the disorder modeled isotropically in another orientation of the isoquinoline ligand, related to the first by 180°, i.e., **20**. The SbF_6 anion is not shown. The numbering differs from that shown in Scheme 4.

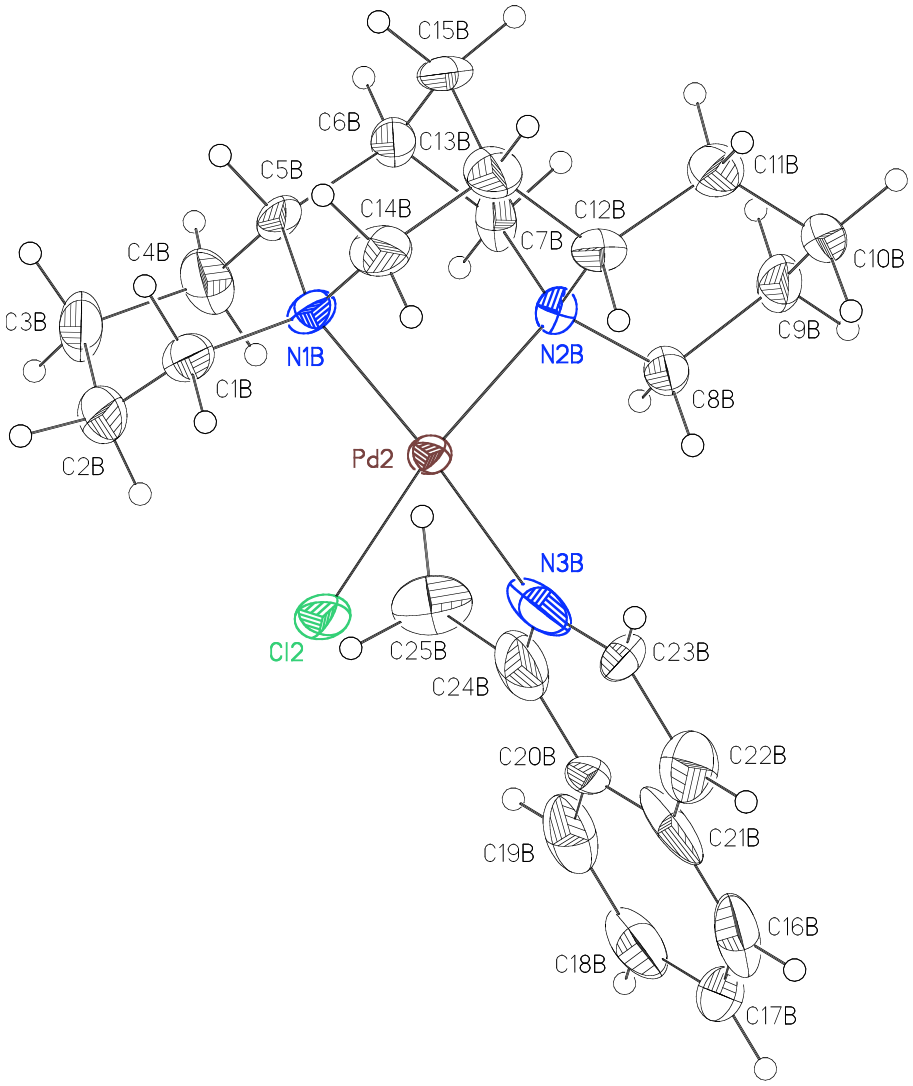

Figure S8. Molecule B of **19/20**. The SbF_6 anion is not shown. The numbering differs from that shown in Scheme 4.

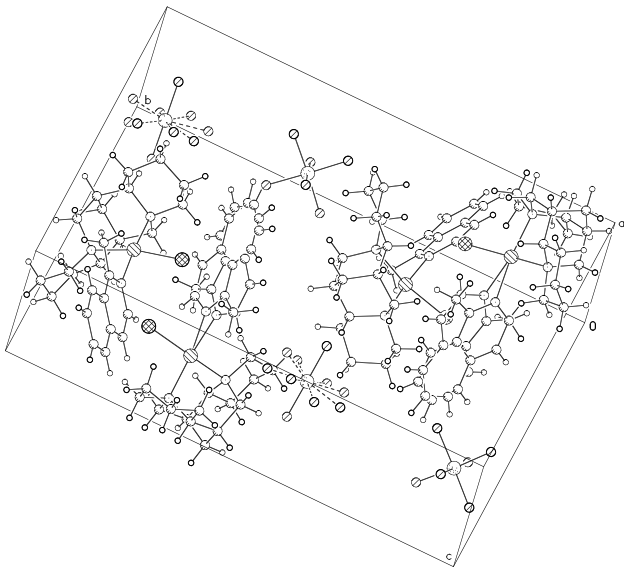

Figure S9. Unit cell contents of **19/20**.

Table S3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **19/20** (CCDC 217276). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Pd(1)	1832(1)	6593(1)	7944(1)	28(1)	1
Cl(1)	2816(2)	7575(1)	8009(1)	67(1)	1
N(1A)	1233(5)	6599(2)	9440(3)	29(1)	1
N(2A)	597(4)	5795(2)	7721(3)	22(1)	1
C(1A)	1873(7)	7099(3)	10106(4)	41(2)	1
C(2A)	3401(7)	7002(3)	10287(4)	41(2)	1
C(3A)	3765(7)	6355(3)	10705(5)	48(2)	1
C(4A)	3042(6)	5864(3)	10044(4)	42(2)	1
C(5A)	1523(6)	5979(3)	9966(4)	32(1)	1
C(6A)	666(6)	5445(3)	9536(4)	34(1)	1
C(7A)	971(6)	5280(2)	8428(4)	26(1)	1
C(8A)	742(5)	5559(2)	6642(4)	27(1)	1
C(9A)	-382(6)	5091(3)	6300(4)	36(1)	1
C(10A)	-1781(6)	5395(3)	6376(4)	38(2)	1
C(11A)	-1956(6)	5592(3)	7449(4)	35(1)	1
C(12A)	-856(5)	6033(2)	7867(4)	24(1)	1
C(13A)	-1094(6)	6183(3)	8973(4)	37(1)	1
C(14A)	-269(6)	6729(3)	9405(4)	37(2)	1
C(15A)	-833(7)	5597(3)	9629(4)	44(2)	1
C(16A)	3596(6)	7149(3)	3531(3)	47(4)	0.471(7)
C(17A)	4830(7)	6914(4)	3189(4)	34(3)	0.471(7)
C(18A)	5641(5)	6537(3)	3819(4)	29(3)	0.471(7)
C(19A)	5218(5)	6395(3)	4791(4)	45(4)	0.471(7)
C(20A)	3984(4)	6631(2)	5133(3)	26(3)	0.471(7)
C(21A)	3173(4)	7008(2)	4503(3)	31(3)	0.471(7)
C(22A)	1938(5)	7244(3)	4844(4)	28(3)	0.471(7)
C(23A)	1515(4)	7102(3)	5816(4)	14(3)	0.471(7)
N(3A)	2326(5)	6725(3)	6447(3)	20(2)	0.471(7)
C(24A)	3561(5)	6490(2)	6105(3)	27(3)	0.471(7)
C(25A)	4390(7)	6146(4)	6816(4)	47(4)	0.471(7)
C(16C)	5473(5)	6425(3)	4151(4)	40(3)	0.529(7)
C(17C)	5178(6)	6774(3)	3284(3)	45(3)	0.529(7)
C(18C)	4002(7)	7142(3)	3229(3)	45(3)	0.529(7)
C(19C)	3122(6)	7161(3)	4041(3)	44(3)	0.529(7)
C(20C)	3418(4)	6812(2)	4909(3)	31(3)	0.529(7)
C(21C)	4594(4)	6444(2)	4964(3)	44(3)	0.529(7)
C(22C)	4889(5)	6095(3)	5831(4)	28(3)	0.529(7)
C(23C)	4010(6)	6114(3)	6644(3)	40(3)	0.529(7)
N(3C)	2834(5)	6482(3)	6589(3)	23(2)	0.529(7)
C(24C)	2538(4)	6831(2)	5721(3)	28(3)	0.529(7)
C(25C)	1549(5)	7149(3)	5583(5)	112(8)	0.529(7)
Pd(2)	6747(1)	8406(1)	7215(1)	23(1)	1
Cl(2)	7697(2)	7416(1)	7135(1)	51(1)	1
N(1B)	6206(4)	8452(2)	5677(3)	27(1)	1
N(2B)	5497(4)	9208(2)	7426(3)	20(1)	1
C(1B)	6883(7)	7967(3)	5029(4)	42(2)	1
C(2B)	8430(7)	8066(3)	4952(5)	47(2)	1
C(3B)	8785(8)	8716(3)	4605(5)	57(2)	1
C(4B)	8070(7)	9192(3)	5273(5)	51(2)	1
C(5B)	6561(7)	9087(3)	5225(4)	41(2)	1
C(6B)	5701(7)	9618(3)	5659(5)	47(2)	1
C(7B)	5940(6)	9742(2)	6787(4)	33(1)	1

C(8B)	5593(5)	9397(3)	8517(4)	27(1)	1
C(9B)	4488(6)	9860(3)	8837(4)	36(1)	1
C(10B)	3080(6)	9571(3)	8661(4)	34(1)	1
C(11B)	2935(6)	9410(3)	7544(4)	39(2)	1
C(12B)	4044(5)	8979(2)	7174(4)	26(1)	1
C(13B)	3866(6)	8874(3)	6036(4)	39(2)	1
C(14B)	4710(6)	8328(3)	5623(4)	41(2)	1
C(15B)	4209(8)	9464(3)	5442(5)	58(2)	1
C(16B)	8608(2)	7857(1)	11686(1)	56(2)	1
C(17B)	9843(2)	8092(1)	12074(1)	58(2)	1
C(18B)	10653(2)	8471(1)	11475(1)	56(2)	1
C(19B)	10228(2)	8614(1)	10488(1)	53(2)	1
C(20B)	8993(2)	8378(1)	10101(1)	47(2)	1
C(21B)	8183(2)	8000(1)	10700(1)	55(2)	1
C(22B)	6949(2)	7764(1)	10312(1)	60(2)	1
C(23B)	6524(2)	7908(1)	9326(1)	39(2)	1
N(3B)	7334(2)	8286(1)	8727(1)	51(2)	1
C(24B)	8568(2)	8522(1)	9114(1)	57(2)	1
C(25B)	9321(2)	8901(1)	8419(1)	48(2)	1
Sb(1)	4944(1)	4157(1)	8114(1)	33(1)	1
F(1A)	6312(1)	4087(1)	7164(1)	71(1)	1
F(2A)	3580(1)	4233(1)	9068(1)	50(1)	1
F(3A)	5543(1)	4958(1)	8534(1)	101(3)	0.855(6)
F(4A)	6017(1)	3788(1)	9070(1)	95(3)	0.855(6)
F(5A)	4243(1)	3421(1)	7628(1)	63(2)	0.855(6)
F(6A)	3832(1)	4574(1)	7165(1)	84(2)	0.855(6)
F(3AB)	4921(1)	4787(1)	7476(1)	92(12)	0.145(6)
F(4AB)	6618(1)	4393(1)	8911(1)	21(5)	0.145(6)
F(5AB)	5340(1)	3303(1)	8584(1)	32(6)	0.145(6)
F(6AB)	3638(1)	3841(1)	7381(1)	60(9)	0.145(6)
Sb(2)	123(1)	925(1)	6831(1)	41(1)	1
F(1B)	-897(1)	1504(1)	7510(1)	73(1)	1
F(2B)	-506(1)	304(1)	7640(1)	95(2)	1
F(3B)	1205(1)	377(1)	6126(1)	154(3)	1
F(4B)	788(1)	1575(1)	6043(1)	129(3)	1
F(5B)	1567(1)	1043(1)	7771(1)	67(1)	1
F(6B)	-1317(1)	792(1)	5887(1)	59(1)	1

Table S4. Bond lengths [Å] and angles [°] for **19/20** (CCDC 217276).

Pd(1)-N(3C)	2.072(4)	C(5A)-C(6A)	1.517(8)
Pd(1)-N(3A)	2.064(4)	C(6A)-C(15A)	1.505(9)
Pd(1)-N(1A)	2.072(4)	C(6A)-C(7A)	1.539(7)
Pd(1)-N(2A)	2.103(4)	C(8A)-C(9A)	1.542(7)
Pd(1)-Cl(1)	2.3056(16)	C(9A)-C(10A)	1.516(8)
N(1A)-C(14A)	1.490(7)	C(10A)-C(11A)	1.491(8)
N(1A)-C(1A)	1.507(7)	C(11A)-C(12A)	1.520(7)
N(1A)-C(5A)	1.518(7)	C(12A)-C(13A)	1.517(7)
N(2A)-C(7A)	1.483(6)	C(13A)-C(14A)	1.518(8)
N(2A)-C(12A)	1.522(6)	C(13A)-C(15A)	1.539(8)
N(2A)-C(8A)	1.520(6)	C(16A)-C(17A)	1.3900
C(1A)-C(2A)	1.517(9)	C(16A)-C(21A)	1.3900
C(2A)-C(3A)	1.527(8)	C(17A)-C(18A)	1.3900
C(3A)-C(4A)	1.524(8)	C(18A)-C(19A)	1.3900
C(4A)-C(5A)	1.502(8)	C(19A)-C(20A)	1.3900

C(20A)-C(21A)	1.3900	Sb(1)-F(5A)	1.8233
C(20A)-C(24A)	1.3900	Sb(1)-F(1A)	1.8592
C(21A)-C(22A)	1.3900	Sb(1)-F(2A)	1.8610
C(22A)-C(23A)	1.3900	Sb(1)-F(6A)	1.8622
C(23A)-N(3A)	1.3900	Sb(1)-F(3A)	1.8852
N(3A)-C(24A)	1.3900	Sb(1)-F(5AB)	1.9618
C(24A)-C(25A)	1.4263	Sb(1)-F(4AB)	1.9850
C(16C)-C(17C)	1.3900	Sb(2)-F(2B)	1.8187
C(16C)-C(21C)	1.3900	Sb(2)-F(1B)	1.8327
C(17C)-C(18C)	1.3900	Sb(2)-F(3B)	1.8431
C(18C)-C(19C)	1.3900	Sb(2)-F(4B)	1.8601
C(19C)-C(20C)	1.3900	Sb(2)-F(5B)	1.8697
C(20C)-C(21C)	1.3900	Sb(2)-F(6B)	1.8748
C(20C)-C(24C)	1.3900		
C(21C)-C(22C)	1.3900	N(3C)-Pd(1)-N(3A)	20.57(18)
C(22C)-C(23C)	1.3900	N(3C)-Pd(1)-N(1A)	166.55(19)
C(23C)-N(3C)	1.3900	N(3A)-Pd(1)-N(1A)	171.34(19)
N(3C)-C(24C)	1.3900	N(3C)-Pd(1)-N(2A)	93.84(19)
C(24C)-C(25C)	1.1893	N(3A)-Pd(1)-N(2A)	97.07(19)
Pd(2)-N(3B)	2.0771(16)	N(1A)-Pd(1)-N(2A)	87.97(16)
Pd(2)-N(1B)	2.087(4)	N(3C)-Pd(1)-Cl(1)	86.08(16)
Pd(2)-N(2B)	2.123(4)	N(3A)-Pd(1)-Cl(1)	78.75(16)
Pd(2)-Cl(2)	2.3110(14)	N(1A)-Pd(1)-Cl(1)	94.91(13)
N(1B)-C(14B)	1.482(7)	N(2A)-Pd(1)-Cl(1)	167.96(13)
N(1B)-C(1B)	1.506(7)	C(14A)-N(1A)-C(1A)	106.2(4)
N(1B)-C(5B)	1.524(7)	C(14A)-N(1A)-C(5A)	110.4(4)
N(2B)-C(7B)	1.488(6)	C(1A)-N(1A)-C(5A)	106.3(4)
N(2B)-C(8B)	1.496(6)	C(14A)-N(1A)-Pd(1)	105.8(3)
N(2B)-C(12B)	1.527(6)	C(1A)-N(1A)-Pd(1)	115.9(3)
C(1B)-C(2B)	1.529(9)	C(5A)-N(1A)-Pd(1)	112.1(3)
C(2B)-C(3B)	1.504(9)	C(7A)-N(2A)-C(12A)	112.5(4)
C(3B)-C(4B)	1.525(8)	C(7A)-N(2A)-C(8A)	108.4(4)
C(4B)-C(5B)	1.488(9)	C(12A)-N(2A)-C(8A)	109.8(4)
C(5B)-C(6B)	1.530(7)	C(7A)-N(2A)-Pd(1)	112.5(3)
C(6B)-C(15B)	1.511(10)	C(12A)-N(2A)-Pd(1)	104.1(3)
C(6B)-C(7B)	1.524(8)	C(8A)-N(2A)-Pd(1)	109.5(3)
C(8B)-C(9B)	1.529(7)	N(1A)-C(1A)-C(2A)	112.7(5)
C(9B)-C(10B)	1.518(8)	C(3A)-C(2A)-C(1A)	113.5(5)
C(10B)-C(11B)	1.516(8)	C(2A)-C(3A)-C(4A)	108.4(5)
C(11B)-C(12B)	1.509(8)	C(5A)-C(4A)-C(3A)	111.6(5)
C(12B)-C(13B)	1.524(7)	C(4A)-C(5A)-N(1A)	110.3(4)
C(13B)-C(15B)	1.524(9)	C(4A)-C(5A)-C(6A)	115.8(5)
C(13B)-C(14B)	1.534(8)	N(1A)-C(5A)-C(6A)	113.0(4)
C(16B)-C(17B)	1.3900	C(15A)-C(6A)-C(5A)	109.5(5)
C(16B)-C(21B)	1.3900	C(15A)-C(6A)-C(7A)	109.8(5)
C(17B)-C(18B)	1.3900	C(5A)-C(6A)-C(7A)	114.2(5)
C(18B)-C(19B)	1.3900	N(2A)-C(7A)-C(6A)	112.2(4)
C(19B)-C(20B)	1.3900	N(2A)-C(8A)-C(9A)	114.0(4)
C(20B)-C(21B)	1.3900	C(10A)-C(9A)-C(8A)	109.7(5)
C(20B)-C(24B)	1.3900	C(11A)-C(10A)-C(9A)	107.9(5)
C(21B)-C(22B)	1.3900	C(10A)-C(11A)-C(12A)	115.0(5)
C(22B)-C(23B)	1.3900	C(13A)-C(12A)-C(11A)	110.9(4)
C(23B)-N(3B)	1.3900	C(13A)-C(12A)-N(2A)	111.0(4)
N(3B)-C(24B)	1.3900	C(11A)-C(12A)-N(2A)	113.5(4)
C(24B)-C(25B)	1.4388	C(14A)-C(13A)-C(12A)	115.5(5)
Sb(1)-F(3AB)	1.5859	C(14A)-C(13A)-C(15A)	109.5(5)
Sb(1)-F(6AB)	1.7176	C(12A)-C(13A)-C(15A)	110.0(5)
Sb(1)-F(4A)	1.8007	N(1A)-C(14A)-C(13A)	112.3(5)

C(6A)-C(15A)-C(13A)	106.1(5)
C(17A)-C(16A)-C(21A)	120.0
C(18A)-C(17A)-C(16A)	120.0
C(17A)-C(18A)-C(19A)	120.0
C(20A)-C(19A)-C(18A)	120.0
C(19A)-C(20A)-C(21A)	120.0
C(19A)-C(20A)-C(24A)	120.0
C(21A)-C(20A)-C(24A)	120.0
C(22A)-C(21A)-C(20A)	120.0
C(22A)-C(21A)-C(16A)	120.0
C(20A)-C(21A)-C(16A)	120.0
C(21A)-C(22A)-C(23A)	120.0
N(3A)-C(23A)-C(22A)	120.0
C(23A)-N(3A)-C(24A)	120.0
C(23A)-N(3A)-Pd(1)	120.6(2)
C(24A)-N(3A)-Pd(1)	119.1(2)
N(3A)-C(24A)-C(20A)	120.0
N(3A)-C(24A)-C(25A)	117.0
C(20A)-C(24A)-C(25A)	122.8
C(17C)-C(16C)-C(21C)	120.0
C(18C)-C(17C)-C(16C)	120.0
C(17C)-C(18C)-C(19C)	120.0
C(18C)-C(19C)-C(20C)	120.0
C(19C)-C(20C)-C(21C)	120.0
C(19C)-C(20C)-C(24C)	120.0
C(21C)-C(20C)-C(24C)	120.0
C(22C)-C(21C)-C(20C)	120.0
C(22C)-C(21C)-C(16C)	120.0
C(20C)-C(21C)-C(16C)	120.0
C(23C)-C(22C)-C(21C)	120.0
C(22C)-C(23C)-N(3C)	120.0
C(24C)-N(3C)-C(23C)	120.0
C(24C)-N(3C)-Pd(1)	123.8(2)
C(23C)-N(3C)-Pd(1)	115.2(2)
C(25C)-C(24C)-N(3C)	125.6
C(25C)-C(24C)-C(20C)	114.3
N(3C)-C(24C)-C(20C)	120.0
N(3B)-Pd(2)-N(1B)	175.35(13)
N(3B)-Pd(2)-N(2B)	96.85(11)
N(1B)-Pd(2)-N(2B)	87.58(16)
N(3B)-Pd(2)-Cl(2)	80.21(6)
N(1B)-Pd(2)-Cl(2)	95.16(13)
N(2B)-Pd(2)-Cl(2)	167.22(12)
C(14B)-N(1B)-C(1B)	107.2(4)
C(14B)-N(1B)-C(5B)	111.9(4)
C(1B)-N(1B)-C(5B)	106.4(4)
C(14B)-N(1B)-Pd(2)	105.2(3)
C(1B)-N(1B)-Pd(2)	114.6(3)
C(5B)-N(1B)-Pd(2)	111.6(3)
C(7B)-N(2B)-C(8B)	109.0(4)
C(7B)-N(2B)-C(12B)	113.8(4)
C(8B)-N(2B)-C(12B)	109.3(4)
C(7B)-N(2B)-Pd(2)	111.6(3)
C(8B)-N(2B)-Pd(2)	108.7(3)
C(12B)-N(2B)-Pd(2)	104.2(3)
N(1B)-C(1B)-C(2B)	112.9(5)
C(3B)-C(2B)-C(1B)	112.5(5)
C(2B)-C(3B)-C(4B)	109.0(5)
C(5B)-C(4B)-C(3B)	110.0(6)
C(4B)-C(5B)-N(1B)	110.6(4)
C(4B)-C(5B)-C(6B)	115.1(6)
N(1B)-C(5B)-C(6B)	112.4(4)
C(15B)-C(6B)-C(7B)	110.3(5)
C(15B)-C(6B)-C(5B)	107.6(6)
C(7B)-C(6B)-C(5B)	115.0(5)
N(2B)-C(7B)-C(6B)	112.3(4)
N(2B)-C(8B)-C(9B)	114.4(4)
C(10B)-C(9B)-C(8B)	109.6(5)
C(11B)-C(10B)-C(9B)	107.6(4)
C(12B)-C(11B)-C(10B)	113.7(5)
C(11B)-C(12B)-N(2B)	113.8(4)
C(11B)-C(12B)-C(13B)	110.1(4)
N(2B)-C(12B)-C(13B)	110.1(4)
C(15B)-C(13B)-C(12B)	111.3(5)
C(15B)-C(13B)-C(14B)	108.5(5)
C(12B)-C(13B)-C(14B)	114.4(5)
N(1B)-C(14B)-C(13B)	112.6(5)
C(6B)-C(15B)-C(13B)	107.8(5)
C(17B)-C(16B)-C(21B)	120.0
C(18B)-C(17B)-C(16B)	120.0
C(17B)-C(18B)-C(19B)	120.0
C(18B)-C(19B)-C(20B)	120.0
C(21B)-C(20B)-C(19B)	120.0
C(21B)-C(20B)-C(24B)	120.0
C(19B)-C(20B)-C(24B)	120.0
C(22B)-C(21B)-C(20B)	120.0
C(22B)-C(21B)-C(16B)	120.0
C(20B)-C(21B)-C(16B)	120.0
C(21B)-C(22B)-C(23B)	120.0
N(3B)-C(23B)-C(22B)	120.0
C(24B)-N(3B)-C(23B)	120.0
C(24B)-N(3B)-Pd(2)	121.60(5)
C(23B)-N(3B)-Pd(2)	118.1
N(3B)-C(24B)-C(20B)	120.0
N(3B)-C(24B)-C(25B)	114.8
C(20B)-C(24B)-C(25B)	125.2
F(3AB)-Sb(1)-F(6AB)	92.0
F(3AB)-Sb(1)-F(4A)	138.0
F(6AB)-Sb(1)-F(4A)	129.2
F(3AB)-Sb(1)-F(5A)	122.9
F(6AB)-Sb(1)-F(5A)	36.6
F(4A)-Sb(1)-F(5A)	94.3
F(3AB)-Sb(1)-F(1A)	73.2
F(6AB)-Sb(1)-F(1A)	97.1
F(4A)-Sb(1)-F(1A)	91.3
F(5A)-Sb(1)-F(1A)	87.9
F(3AB)-Sb(1)-F(2A)	106.5
F(6AB)-Sb(1)-F(2A)	83.3
F(4A)-Sb(1)-F(2A)	88.7
F(5A)-Sb(1)-F(2A)	92.6
F(1A)-Sb(1)-F(2A)	179.5
F(3AB)-Sb(1)-F(6A)	40.4
F(6AB)-Sb(1)-F(6A)	53.0
F(4A)-Sb(1)-F(6A)	177.2
F(5A)-Sb(1)-F(6A)	88.2
F(1A)-Sb(1)-F(6A)	90.0

F(2A)-Sb(1)-F(6A)	90.0	F(1A)-Sb(1)-F(4AB)	77.5
F(3AB)-Sb(1)-F(3A)	52.2	F(2A)-Sb(1)-F(4AB)	102.2
F(6AB)-Sb(1)-F(3A)	137.9	F(6A)-Sb(1)-F(4AB)	133.9
F(4A)-Sb(1)-F(3A)	91.2	F(3A)-Sb(1)-F(4AB)	50.9
F(5A)-Sb(1)-F(3A)	174.5	F(5AB)-Sb(1)-F(4AB)	85.1
F(1A)-Sb(1)-F(3A)	92.8	F(2B)-Sb(2)-F(1B)	90.6
F(2A)-Sb(1)-F(3A)	86.8	F(2B)-Sb(2)-F(3B)	92.2
F(6A)-Sb(1)-F(3A)	86.3	F(1B)-Sb(2)-F(3B)	177.0
F(3AB)-Sb(1)-F(5AB)	162.9	F(2B)-Sb(2)-F(4B)	178.1
F(6AB)-Sb(1)-F(5AB)	87.2	F(1B)-Sb(2)-F(4B)	88.4
F(4A)-Sb(1)-F(5AB)	42.7	F(3B)-Sb(2)-F(4B)	88.8
F(5A)-Sb(1)-F(5AB)	51.6	F(2B)-Sb(2)-F(5B)	88.2
F(1A)-Sb(1)-F(5AB)	90.0	F(1B)-Sb(2)-F(5B)	89.7
F(2A)-Sb(1)-F(5AB)	90.3	F(3B)-Sb(2)-F(5B)	89.3
F(6A)-Sb(1)-F(5AB)	139.8	F(4B)-Sb(2)-F(5B)	90.2
F(3A)-Sb(1)-F(5AB)	133.8	F(2B)-Sb(2)-F(6B)	91.2
F(3AB)-Sb(1)-F(4AB)	93.8	F(1B)-Sb(2)-F(6B)	91.2
F(6AB)-Sb(1)-F(4AB)	170.5	F(3B)-Sb(2)-F(6B)	89.8
F(4A)-Sb(1)-F(4AB)	44.3	F(4B)-Sb(2)-F(6B)	90.4
F(5A)-Sb(1)-F(4AB)	134.5	F(5B)-Sb(2)-F(6B)	179.0

X-ray crystallographic structure for **[(sparteine)Pd(2-mesitlypyridine)Cl]$^+$SbF$_6^-$ (24)**. The crystallographic data for **24** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 215758.

Crystal data and structural refinement for 24 (CCDC 215758).

Empirical formula	$[C_{29}H_{41}N_3ClPd]^+ [SbF_6]^-$
Formula weight	809.25
Crystallization Solvent	Acetone/pentane
Crystal Habit	Block
Crystal size	0.30 x 0.30 x 0.26 mm^3
Crystal color	Clear
Data Collection	
Preliminary Photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 41762 reflections used in lattice determination	2.27 to 40.10°
Unit cell dimensions	a = 12.3773(2) Å b = 13.1425(2) Å c = 18.7060(3) Å
Volume	3042.88(8) Å^3
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.766 Mg/m^3
F(000)	1616
Data collection program	Bruker SMART v5.054
θ range for data collection	1.89 to 40.43°
Completeness to θ = 40.43°	96.5 %
Index ranges	$-22 \le h \le 22$, $-22 \le k \le 23$, $-33 \le l \le 32$
Data collection scan type	ω scans at 3 ϕ settings each for two 2θ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	77220
Independent reflections	18496 [R_{int}= 0.0639]
Absorption coefficient	1.628 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.6769 and 0.6409
Structure solution and Refinement	
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	18496 / 0 / 534
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.165
Final R indices [I>2σ(I), 15330 reflections]	R1 = 0.0313, *w*R2 = 0.0489
R indices (all data)	R1 = 0.0450, *w*R2 = 0.0507
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.003
Average shift/error	0.000
Absolute structure parameter	-0.036(8)
Largest diff. peak and hole	2.104 and -0.833 e.Å^{-3}

Special Refinement Details

All peaks in the final difference Fourier map greater than $1e^{-}/Å^3$ are within 1Å of either Pd or Sb.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

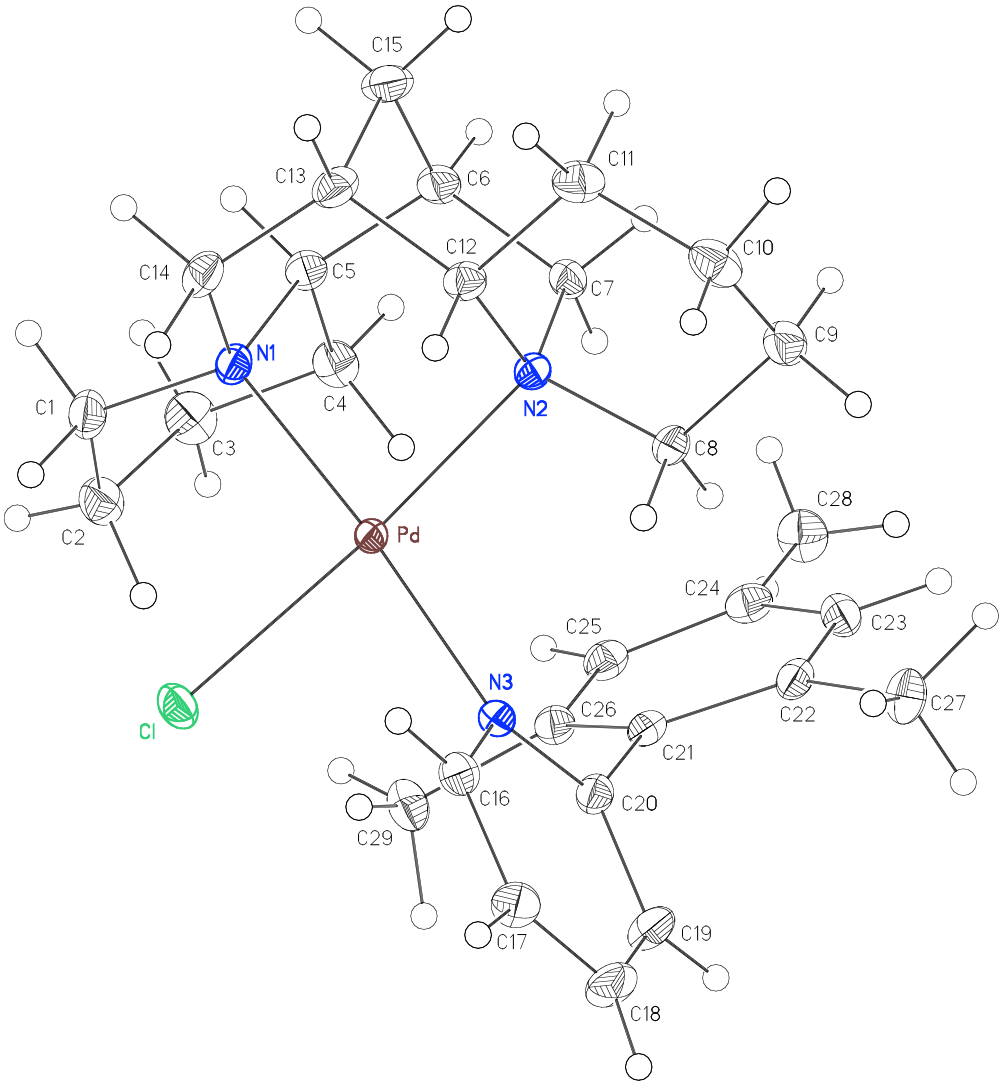

Figure S10. Molecule of **24**. The SbF_6 anion is not shown.

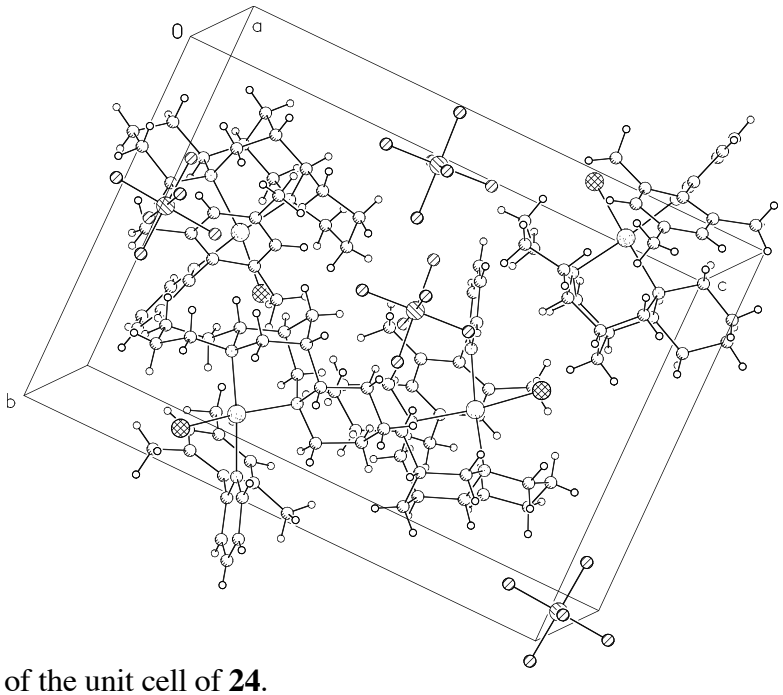

Figure S11. Contents of the unit cell of **24**.

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **24** (CCDC 215758). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd	7977(1)	9200(1)	2910(1)	10(1)
Cl	8780(1)	10248(1)	2054(1)	18(1)
N(1)	8300(1)	7866(1)	2338(1)	14(1)
N(2)	7698(1)	8262(1)	3822(1)	12(1)
N(3)	7646(1)	10586(1)	3401(1)	12(1)
C(1)	8532(2)	8028(2)	1554(1)	19(1)
C(2)	7571(2)	8421(2)	1130(1)	20(1)
C(3)	6574(2)	7756(2)	1229(1)	22(1)
C(4)	6378(1)	7573(1)	2025(1)	18(1)
C(5)	7371(1)	7116(1)	2374(1)	16(1)
C(6)	7197(1)	6700(1)	3124(1)	16(1)
C(7)	6853(1)	7483(1)	3677(1)	14(1)
C(8)	7347(1)	8917(1)	4438(1)	14(1)
C(9)	7344(1)	8399(1)	5168(1)	19(1)
C(10)	8471(2)	8001(2)	5335(1)	21(1)
C(11)	8835(2)	7301(1)	4739(1)	20(1)
C(12)	8785(1)	7789(1)	3989(1)	15(1)
C(13)	9104(1)	7003(1)	3420(1)	17(1)
C(14)	9294(1)	7433(1)	2678(1)	18(1)
C(15)	8234(2)	6168(1)	3368(1)	20(1)
C(16)	8539(1)	11119(1)	3575(1)	15(1)
C(17)	8500(2)	12106(1)	3823(1)	19(1)
C(18)	7512(2)	12579(2)	3875(1)	21(1)
C(19)	6591(2)	12036(1)	3703(1)	19(1)
C(20)	6668(1)	11035(1)	3475(1)	14(1)
C(21)	5660(1)	10427(1)	3337(1)	12(1)
C(22)	4994(1)	10172(1)	3923(1)	14(1)

C(23)	4067(1)	9586(1)	3788(1)	16(1)
C(24)	3775(1)	9282(1)	3107(1)	16(1)
C(25)	4421(1)	9595(1)	2536(1)	15(1)
C(26)	5344(1)	10178(1)	2639(1)	14(1)
C(27)	5200(1)	10522(2)	4674(1)	19(1)
C(28)	2766(1)	8665(2)	2979(1)	21(1)
C(29)	5902(1)	10624(2)	1993(1)	19(1)
Sb	6064(1)	4630(1)	5153(1)	16(1)
F(1)	4576(1)	4858(1)	5179(1)	35(1)
F(2)	6099(1)	4534(1)	6155(1)	25(1)
F(3)	7550(1)	4388(1)	5096(1)	30(1)
F(4)	6037(1)	4736(1)	4153(1)	31(1)
F(5)	5796(1)	3231(1)	5090(1)	24(1)
F(6)	6316(1)	6030(1)	5228(1)	40(1)

Table S6. Selected bond lengths [Å] and angles [°] for **24** (CCDC 215758).

Pd-N(3)	2.0809(13)	C(10)-H(10B)	0.96(2)
Pd-N(1)	2.0914(14)	C(11)-C(12)	1.544(2)
Pd-N(2)	2.1326(14)	C(11)-H(11A)	1.00(2)
Pd-Cl	2.3345(4)	C(11)-H(11B)	0.98(2)
N(1)-C(14)	1.497(2)	C(12)-C(13)	1.535(2)
N(1)-C(1)	1.509(2)	C(12)-H(12)	0.92(2)
N(1)-C(5)	1.517(2)	C(13)-C(14)	1.516(3)
N(2)-C(7)	1.488(2)	C(13)-C(15)	1.540(3)
N(2)-C(8)	1.503(2)	C(13)-H(13)	0.956(18)
N(2)-C(12)	1.515(2)	C(14)-H(14A)	1.00(2)
N(3)-C(16)	1.348(2)	C(14)-H(14B)	0.97(2)
N(3)-C(20)	1.355(2)	C(15)-H(15A)	0.93(2)
C(1)-C(2)	1.519(3)	C(15)-H(15B)	0.96(2)
C(1)-H(1A)	0.92(2)	C(16)-C(17)	1.379(2)
C(1)-H(1B)	1.01(2)	C(16)-H(16)	0.877(19)
C(2)-C(3)	1.524(3)	C(17)-C(18)	1.375(3)
C(2)-H(2A)	0.94(2)	C(17)-H(17)	0.93(3)
C(2)-H(2B)	0.85(2)	C(18)-C(19)	1.383(3)
C(3)-C(4)	1.528(3)	C(18)-H(18)	0.83(2)
C(3)-H(3A)	0.92(2)	C(19)-C(20)	1.385(2)
C(3)-H(3B)	0.95(2)	C(19)-H(19)	0.89(2)
C(4)-C(5)	1.515(2)	C(20)-C(21)	1.503(2)
C(4)-H(4A)	0.97(2)	C(21)-C(26)	1.401(2)
C(4)-H(4B)	0.91(2)	C(21)-C(22)	1.413(2)
C(5)-C(6)	1.522(2)	C(22)-C(23)	1.404(2)
C(5)-H(5)	0.95(2)	C(22)-C(27)	1.499(2)
C(6)-C(7)	1.518(2)	C(23)-C(24)	1.384(2)
C(6)-C(15)	1.531(2)	C(23)-H(23)	0.94(2)
C(6)-H(6)	0.99(2)	C(24)-C(25)	1.396(2)
C(7)-H(7A)	0.85(2)	C(24)-C(28)	1.508(2)
C(7)-H(7B)	0.891(19)	C(25)-C(26)	1.389(2)
C(8)-C(9)	1.526(3)	C(25)-H(25)	0.95(2)
C(8)-H(8A)	0.937(18)	C(26)-C(29)	1.511(2)
C(8)-H(8B)	0.93(2)	C(27)-H(27A)	0.91(2)
C(9)-C(10)	1.522(3)	C(27)-H(27B)	1.03(3)
C(9)-H(9A)	0.89(2)	C(27)-H(27C)	0.94(3)
C(9)-H(9B)	0.92(2)	C(28)-H(28A)	0.85(2)
C(10)-C(11)	1.515(3)	C(28)-H(28B)	1.02(3)
C(10)-H(10A)	0.82(2)	C(28)-H(28C)	0.85(3)

C(29)-H(29A)	0.94(2)	C(4)-C(5)-H(5)	108.3(12)
C(29)-H(29B)	0.85(2)	C(6)-C(5)-H(5)	106.3(13)
C(29)-H(29C)	1.01(3)	C(7)-C(6)-C(5)	115.08(14)
Sb-F(1)	1.8662(11)	C(7)-C(6)-C(15)	110.01(14)
Sb-F(3)	1.8697(10)	C(5)-C(6)-C(15)	108.66(14)
Sb-F(5)	1.8716(11)	C(7)-C(6)-H(6)	103.4(13)
Sb-F(6)	1.8720(12)	C(5)-C(6)-H(6)	105.0(14)
Sb-F(4)	1.8753(10)	C(15)-C(6)-H(6)	114.7(13)
Sb-F(2)	1.8794(10)	N(2)-C(7)-C(6)	113.19(13)
N(3)-Pd-N(1)	175.42(5)	N(2)-C(7)-H(7A)	104.5(13)
N(3)-Pd-N(2)	96.95(5)	C(6)-C(7)-H(7A)	112.2(14)
N(1)-Pd-N(2)	87.48(5)	N(2)-C(7)-H(7B)	112.7(12)
N(3)-Pd-Cl	82.53(4)	C(6)-C(7)-H(7B)	107.3(12)
N(1)-Pd-Cl	93.56(4)	H(7A)-C(7)-H(7B)	106.9(17)
N(2)-Pd-Cl	163.51(4)	N(2)-C(8)-C(9)	115.59(14)
C(14)-N(1)-C(1)	108.07(13)	N(2)-C(8)-H(8A)	105.7(12)
C(14)-N(1)-C(5)	110.91(13)	C(9)-C(8)-H(8A)	112.1(11)
C(1)-N(1)-C(5)	106.14(13)	N(2)-C(8)-H(8B)	107.6(13)
C(14)-N(1)-Pd	105.02(10)	C(9)-C(8)-H(8B)	109.3(13)
C(1)-N(1)-Pd	114.53(11)	H(8A)-C(8)-H(8B)	106.0(17)
C(5)-N(1)-Pd	112.17(10)	C(10)-C(9)-C(8)	109.59(15)
C(7)-N(2)-C(8)	109.35(12)	C(10)-C(9)-H(9A)	111.0(15)
C(7)-N(2)-C(12)	112.26(13)	C(8)-C(9)-H(9A)	116.2(16)
C(8)-N(2)-C(12)	109.49(12)	C(10)-C(9)-H(9B)	108.7(13)
C(7)-N(2)-Pd	111.44(10)	C(8)-C(9)-H(9B)	105.6(14)
C(8)-N(2)-Pd	109.25(10)	H(9A)-C(9)-H(9B)	105(2)
C(12)-N(2)-Pd	104.94(9)	C(11)-C(10)-C(9)	109.29(15)
C(16)-N(3)-C(20)	118.76(14)	C(11)-C(10)-H(10A)	109.7(16)
C(16)-N(3)-Pd	113.61(11)	C(9)-C(10)-H(10A)	110.8(15)
C(20)-N(3)-Pd	127.09(11)	C(11)-C(10)-H(10B)	106.5(12)
N(1)-C(1)-C(2)	113.97(14)	C(9)-C(10)-H(10B)	115.7(11)
N(1)-C(1)-H(1A)	108.7(14)	H(10A)-C(10)-H(10B)	104.6(19)
C(2)-C(1)-H(1A)	110.3(14)	C(10)-C(11)-C(12)	113.93(15)
N(1)-C(1)-H(1B)	110.8(12)	C(10)-C(11)-H(11A)	104.6(14)
C(2)-C(1)-H(1B)	109.5(11)	C(12)-C(11)-H(11A)	110.5(14)
H(1A)-C(1)-H(1B)	103.0(17)	C(10)-C(11)-H(11B)	111.5(13)
C(1)-C(2)-C(3)	112.13(16)	C(12)-C(11)-H(11B)	106.4(13)
C(1)-C(2)-H(2A)	112.8(14)	H(11A)-C(11)-H(11B)	110.0(17)
C(3)-C(2)-H(2A)	109.0(13)	N(2)-C(12)-C(13)	111.18(13)
C(1)-C(2)-H(2B)	111.1(14)	N(2)-C(12)-C(11)	113.15(14)
C(3)-C(2)-H(2B)	107.0(15)	C(13)-C(12)-C(11)	109.96(14)
H(2A)-C(2)-H(2B)	104(2)	N(2)-C(12)-H(12)	106.5(12)
C(2)-C(3)-C(4)	109.62(15)	C(13)-C(12)-H(12)	111.6(13)
C(2)-C(3)-H(3A)	110.2(14)	C(11)-C(12)-H(12)	104.2(13)
C(4)-C(3)-H(3A)	104.5(14)	C(14)-C(13)-C(12)	115.11(15)
C(2)-C(3)-H(3B)	107.3(14)	C(14)-C(13)-C(15)	108.42(15)
C(4)-C(3)-H(3B)	111.7(14)	C(12)-C(13)-C(15)	110.11(14)
H(3A)-C(3)-H(3B)	113.6(19)	C(14)-C(13)-H(13)	109.8(11)
C(5)-C(4)-C(3)	110.71(15)	C(12)-C(13)-H(13)	104.7(11)
C(5)-C(4)-H(4A)	113.7(12)	C(15)-C(13)-H(13)	108.4(11)
C(3)-C(4)-H(4A)	110.0(12)	N(1)-C(14)-C(13)	113.76(13)
C(5)-C(4)-H(4B)	106.8(13)	N(1)-C(14)-H(14A)	105.3(12)
C(3)-C(4)-H(4B)	113.5(15)	C(13)-C(14)-H(14A)	116.2(12)
H(4A)-C(4)-H(4B)	101.8(18)	N(1)-C(14)-H(14B)	105.3(11)
N(1)-C(5)-C(4)	109.80(14)	C(13)-C(14)-H(14B)	110.3(11)
N(1)-C(5)-C(6)	112.37(14)	H(14A)-C(14)-H(14B)	105.2(16)
C(4)-C(5)-C(6)	115.16(14)	C(6)-C(15)-C(13)	106.20(14)
N(1)-C(5)-H(5)	104.1(12)	C(6)-C(15)-H(15A)	115.2(13)

C(13)-C(15)-H(15A)	109.7(13)	C(25)-C(26)-C(29)	118.55(15)
C(6)-C(15)-H(15B)	110.4(11)	C(21)-C(26)-C(29)	121.77(15)
C(13)-C(15)-H(15B)	111.2(11)	C(22)-C(27)-H(27A)	118.7(16)
H(15A)-C(15)-H(15B)	104.1(17)	C(22)-C(27)-H(27B)	109.5(13)
N(3)-C(16)-C(17)	122.84(16)	H(27A)-C(27)-H(27B)	111(2)
N(3)-C(16)-H(16)	116.9(13)	C(22)-C(27)-H(27C)	112.9(16)
C(17)-C(16)-H(16)	120.2(13)	H(27A)-C(27)-H(27C)	102(2)
C(18)-C(17)-C(16)	118.69(16)	H(27B)-C(27)-H(27C)	100.9(19)
C(18)-C(17)-H(17)	125.7(16)	C(24)-C(28)-H(28A)	115.3(15)
C(16)-C(17)-H(17)	115.4(16)	C(24)-C(28)-H(28B)	113.5(17)
C(17)-C(18)-C(19)	118.84(17)	H(28A)-C(28)-H(28B)	99(2)
C(17)-C(18)-H(18)	118.2(15)	C(24)-C(28)-H(28C)	113.1(16)
C(19)-C(18)-H(18)	122.9(15)	H(28A)-C(28)-H(28C)	104(2)
C(18)-C(19)-C(20)	120.36(17)	H(28B)-C(28)-H(28C)	111(2)
C(18)-C(19)-H(19)	119.2(13)	C(26)-C(29)-H(29A)	114.8(13)
C(20)-C(19)-H(19)	120.4(14)	C(26)-C(29)-H(29B)	116.7(15)
N(3)-C(20)-C(19)	120.44(15)	H(29A)-C(29)-H(29B)	105.0(18)
N(3)-C(20)-C(21)	119.50(14)	C(26)-C(29)-H(29C)	110.5(17)
C(19)-C(20)-C(21)	120.02(15)	H(29A)-C(29)-H(29C)	111(2)
C(26)-C(21)-C(22)	120.24(14)	H(29B)-C(29)-H(29C)	97(2)
C(26)-C(21)-C(20)	121.10(14)	F(1)-Sb-F(3)	178.15(6)
C(22)-C(21)-C(20)	118.51(14)	F(1)-Sb-F(5)	89.11(5)
C(23)-C(22)-C(21)	117.88(14)	F(3)-Sb-F(5)	90.21(5)
C(23)-C(22)-C(27)	118.47(14)	F(1)-Sb-F(6)	90.27(6)
C(21)-C(22)-C(27)	123.62(15)	F(3)-Sb-F(6)	90.43(6)
C(24)-C(23)-C(22)	122.49(15)	F(5)-Sb-F(6)	179.07(6)
C(24)-C(23)-H(23)	120.7(14)	F(1)-Sb-F(4)	89.79(5)
C(22)-C(23)-H(23)	116.8(14)	F(3)-Sb-F(4)	88.49(5)
C(23)-C(24)-C(25)	118.05(15)	F(5)-Sb-F(4)	90.41(5)
C(23)-C(24)-C(28)	121.12(16)	F(6)-Sb-F(4)	90.28(6)
C(25)-C(24)-C(28)	120.79(16)	F(1)-Sb-F(2)	90.41(5)
C(26)-C(25)-C(24)	121.77(15)	F(3)-Sb-F(2)	91.32(5)
C(26)-C(25)-H(25)	121.5(12)	F(5)-Sb-F(2)	90.05(5)
C(24)-C(25)-H(25)	116.7(12)	F(6)-Sb-F(2)	89.27(5)
C(25)-C(26)-C(21)	119.29(15)	F(4)-Sb-F(2)	179.50(5)

X-ray crystallographic structure for **[(sparteine)Pd(*S*-OCH(CF_3)C_6H_5)Cl (31)**. The crystallographic data for **31** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 222289.

Crystal data and structural refinement for 31 (CCDC 222289).

Empirical formula	$C_{23}H_{32}ClF_3N_2OPd \cdot 2CH_2Cl_2$
Formula weight	721.21
Crystallization solvent	Dichloromethane/hexane
Crystal habit	Block
Crystal size	0.33 x 0.33 x 0.26 mm^3
Crystal color	Orange

Data collection

Preliminary photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 30297 reflections used in lattice determination	2.35 to 38.68°
Unit cell dimensions	a = 14.8633(3) Å b = 13.4427(3) Å β = 98.5410(10)° c = 15.0189(3) Å
Volume	2967.54(11) $Å^3$
Z	4
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.614 Mg/m^3
F(000)	1464
Data collection program	Bruker SMART v5.054
θ range for data collection	1.80 to 40.44°
Completeness to θ = 40.44°	93.7 %
Index ranges	$-26 \le h \le 26$, $-24 \le k \le 24$, $-27 \le l \le 27$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.022
Reflections collected	79009
Independent reflections	33021 [R_{int}= 0.0654]
Absorption coefficient	1.117 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.7600 and 0.7094

Structure solution and refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	33021 / 1 / 667
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	0.987
Final R indices [I>2σ(I), 21505 reflections]	R1 = 0.0401, *w*R2 = 0.0608
R indices (all data)	R1 = 0.0826, *w*R2 = 0.0669
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.003

Average shift/error	0.000
Absolute structure parameter	-0.036(10)
Largest diff. peak and hole	2.072 and -1.257 e.Å^{-3}

Special refinement details

Peaks in the difference Fourier larger than 1e$^-$/Å^3 lie near metal centers or near solvent molecules.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

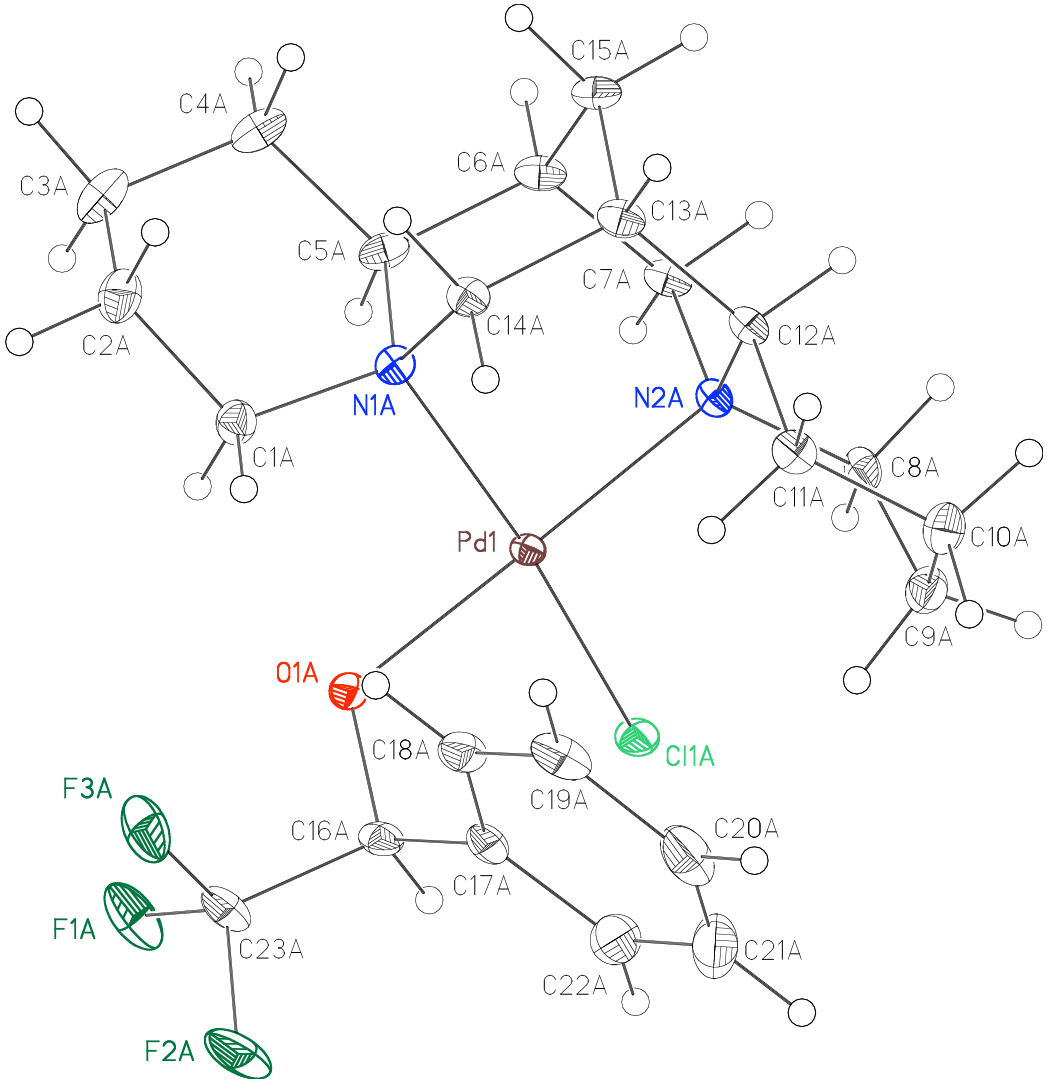

Figure S12. Molecule A of **31**.

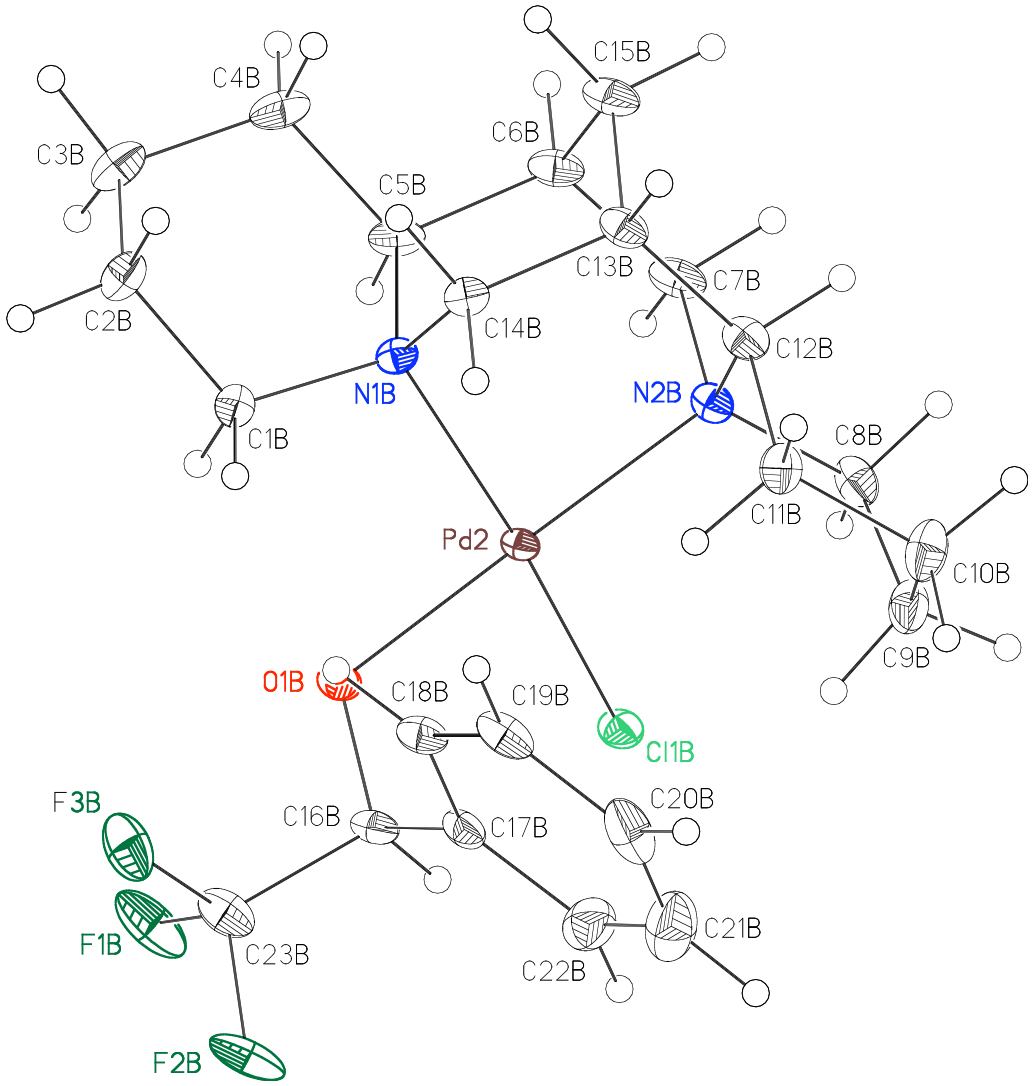

Figure S13. Molecule B of **31**.

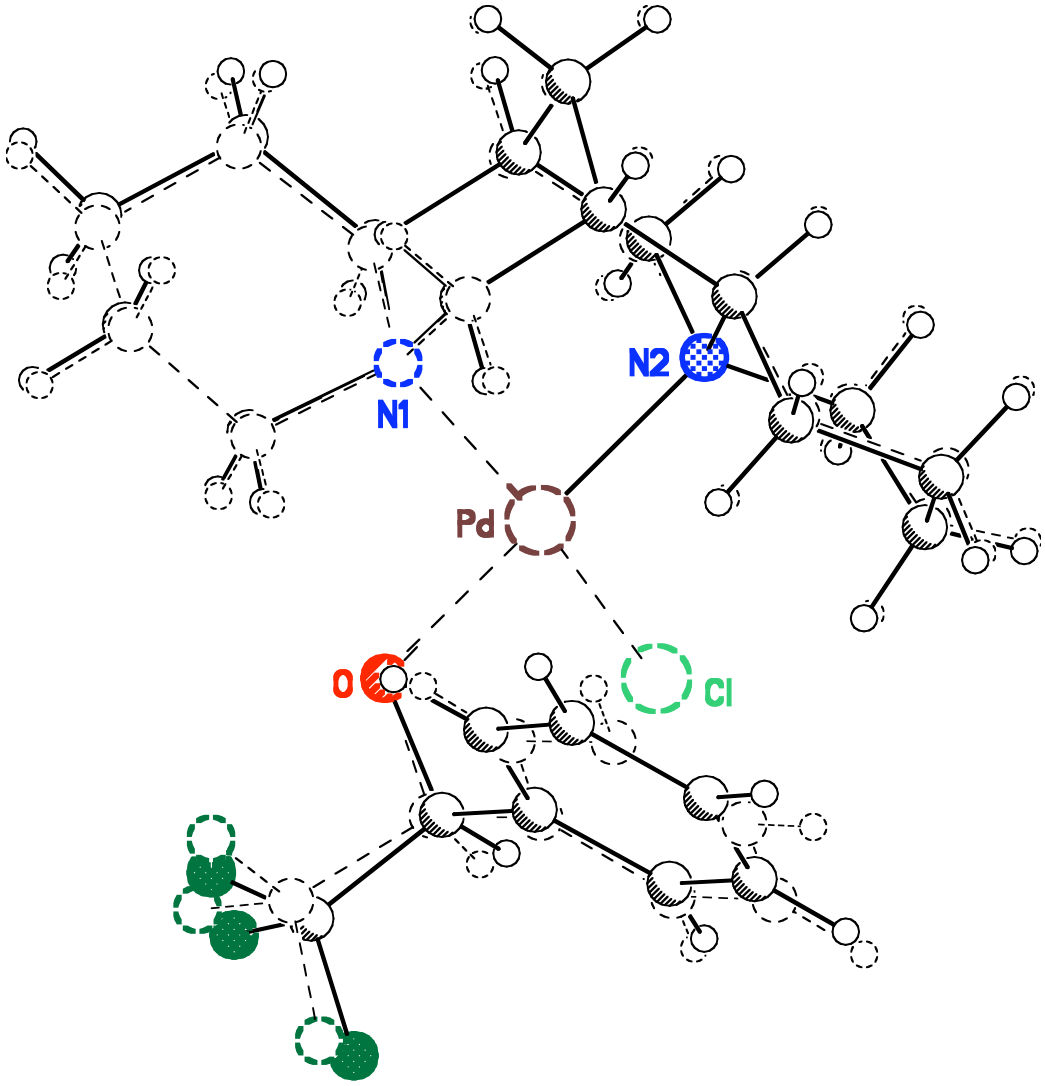

Figure S14. Overlay of molecules A and B of **31**.

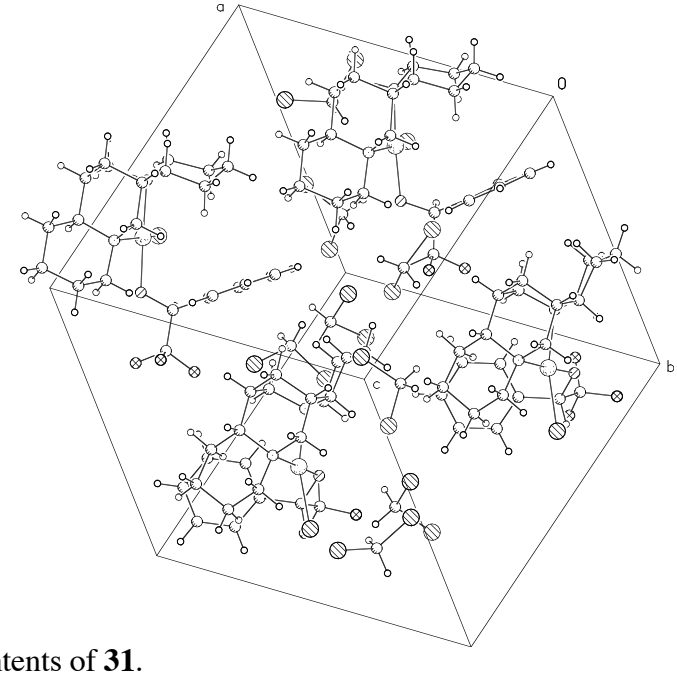

Figure S15. Unit cell contents of **31**.

Table S7 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **31** (CCDC 222289). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	9658(1)	1631(1)	6561(1)	9(1)
Cl(1A)	10145(1)	2782(1)	5574(1)	15(1)
F(1A)	9805(1)	4511(1)	8328(1)	27(1)
F(2A)	8480(1)	5031(1)	7720(1)	29(1)
F(3A)	8599(1)	3725(1)	8568(1)	25(1)
O(1A)	9590(1)	2755(1)	7422(1)	13(1)
N(1A)	9586(1)	600(1)	7620(1)	10(1)
N(2A)	9650(1)	419(1)	5686(1)	10(1)
C(1A)	9524(1)	1159(2)	8481(1)	15(1)
C(2A)	9673(2)	521(2)	9325(1)	19(1)
C(3A)	10620(2)	66(2)	9425(2)	22(1)
C(4A)	10706(2)	-538(2)	8589(1)	19(1)
C(5A)	10482(1)	41(2)	7711(1)	14(1)
C(6A)	10505(1)	-655(1)	6901(1)	14(1)
C(7A)	10509(1)	-141(1)	5999(1)	13(1)
C(8A)	9648(1)	690(2)	4709(1)	13(1)
C(9A)	8793(1)	1235(2)	4292(1)	17(1)
C(10A)	7926(1)	666(2)	4410(1)	17(1)
C(11A)	7963(1)	370(2)	5397(1)	14(1)
C(12A)	8824(1)	-232(1)	5714(1)	12(1)
C(13A)	8843(1)	-756(2)	6615(1)	14(1)
C(14A)	8780(1)	-70(1)	7411(1)	13(1)
C(15A)	9707(1)	-1382(1)	6810(1)	14(1)
C(16A)	9043(1)	3566(1)	7101(1)	13(1)
C(17A)	8105(1)	3301(1)	6612(1)	14(1)
C(18A)	7536(1)	2645(1)	6981(2)	16(1)
C(19A)	6681(2)	2399(2)	6525(2)	22(1)
C(20A)	6387(2)	2824(2)	5686(2)	28(1)
C(21A)	6944(2)	3467(2)	5305(2)	29(1)
C(22A)	7795(2)	3698(2)	5770(2)	22(1)
C(23A)	8981(2)	4202(2)	7923(2)	18(1)
Pd(2)	5335(1)	6767(1)	8409(1)	9(1)
Cl(1B)	4743(1)	7843(1)	9400(1)	15(1)
F(1B)	5357(1)	9923(1)	7127(1)	32(1)
F(2B)	6682(1)	10294(1)	7854(1)	31(1)
F(3B)	6559(1)	9240(1)	6755(1)	27(1)
O(1B)	5545(1)	7965(1)	7666(1)	14(1)
N(1B)	5470(1)	5806(1)	7313(1)	11(1)
N(2B)	5260(1)	5492(1)	9195(1)	12(1)
C(1B)	5580(1)	6435(1)	6501(1)	14(1)
C(2B)	5487(1)	5866(2)	5610(1)	18(1)
C(3B)	4556(2)	5373(2)	5418(2)	22(1)
C(4B)	4431(2)	4708(2)	6215(2)	20(1)
C(5B)	4574(1)	5242(2)	7128(1)	16(1)
C(6B)	4490(1)	4491(2)	7883(2)	17(1)
C(7B)	4422(1)	4946(2)	8799(2)	17(1)
C(8B)	5199(1)	5700(2)	10174(1)	17(1)
C(9B)	6035(2)	6214(2)	10670(1)	20(1)
C(10B)	6910(2)	5644(2)	10592(1)	21(1)
C(11B)	6950(1)	5421(2)	9600(1)	17(1)
C(12B)	6099(1)	4845(2)	9190(1)	15(1)
C(13B)	6149(2)	4388(2)	8271(2)	15(1)

C(14B)	6264(1)	5127(1)	7525(1)	13(1)
C(15B)	5293(1)	3763(2)	7987(2)	19(1)
C(16B)	6090(1)	8699(1)	8131(2)	14(1)
C(17B)	7021(1)	8338(1)	8570(1)	14(1)
C(18B)	7542(1)	7725(1)	8102(2)	16(1)
C(19B)	8389(2)	7381(2)	8508(2)	20(1)
C(20B)	8727(2)	7661(2)	9384(2)	26(1)
C(21B)	8221(2)	8277(2)	9851(2)	31(1)
C(22B)	7369(2)	8607(2)	9446(2)	24(1)
C(23B)	6174(2)	9530(2)	7470(2)	20(1)
Cl(1)	2364(1)	2484(1)	7629(1)	42(1)
Cl(2)	2011(1)	4589(1)	7957(1)	28(1)
C(1)	1617(2)	3498(2)	7362(2)	25(1)
Cl(3)	2857(1)	7766(1)	7195(1)	35(1)
Cl(4)	3021(1)	9919(1)	6994(1)	27(1)
C(2)	3595(2)	8794(2)	7351(2)	27(1)
Cl(5)	8073(1)	6412(1)	6004(1)	29(1)
Cl(6)	7021(1)	7850(1)	4830(1)	38(1)
C(3)	7710(2)	6783(2)	4890(2)	25(1)
Cl(7)	8491(1)	1853(1)	1115(1)	50(1)
Cl(8)	7230(1)	1720(1)	-585(1)	54(1)
C(4)	7657(2)	2468(2)	337(2)	43(1)

Table S8. Bond lengths [Å] and angles [°] for **31** (CCDC 222289).

Pd(1)-O(1A)	2.0012(14)	C(13A)-C(15A)	1.527(3)
Pd(1)-N(2A)	2.0925(16)	C(16A)-C(23A)	1.515(3)
Pd(1)-N(1A)	2.1243(17)	C(16A)-C(17A)	1.519(3)
Pd(1)-Cl(1A)	2.3316(5)	C(17A)-C(22A)	1.387(3)
F(1A)-C(23A)	1.350(2)	C(17A)-C(18A)	1.393(3)
F(2A)-C(23A)	1.349(2)	C(18A)-C(19A)	1.390(3)
F(3A)-C(23A)	1.355(2)	C(19A)-C(20A)	1.393(3)
O(1A)-C(16A)	1.402(2)	C(20A)-C(21A)	1.379(4)
N(1A)-C(14A)	1.494(2)	C(21A)-C(22A)	1.385(3)
N(1A)-C(1A)	1.510(2)	Pd(2)-O(1B)	2.0101(14)
N(1A)-C(5A)	1.518(2)	Pd(2)-N(2B)	2.0936(16)
N(2A)-C(7A)	1.496(2)	Pd(2)-N(1B)	2.1260(16)
N(2A)-C(8A)	1.511(2)	Pd(2)-Cl(1B)	2.3384(5)
N(2A)-C(12A)	1.515(2)	F(1B)-C(23B)	1.353(2)
C(1A)-C(2A)	1.519(3)	F(2B)-C(23B)	1.352(2)
C(2A)-C(3A)	1.521(3)	F(3B)-C(23B)	1.348(2)
C(3A)-C(4A)	1.517(3)	O(1B)-C(16B)	1.396(2)
C(4A)-C(5A)	1.525(3)	N(1B)-C(14B)	1.488(2)
C(5A)-C(6A)	1.539(3)	N(1B)-C(1B)	1.513(2)
C(6A)-C(7A)	1.522(3)	N(1B)-C(5B)	1.522(2)
C(6A)-C(15A)	1.527(3)	N(2B)-C(7B)	1.492(3)
C(8A)-C(9A)	1.519(3)	N(2B)-C(8B)	1.512(3)
C(9A)-C(10A)	1.531(3)	N(2B)-C(12B)	1.521(2)
C(10A)-C(11A)	1.527(3)	C(1B)-C(2B)	1.528(3)
C(11A)-C(12A)	1.529(3)	C(2B)-C(3B)	1.522(3)
C(12A)-C(13A)	1.523(3)	C(3B)-C(4B)	1.527(3)
C(13A)-C(14A)	1.522(3)	C(4B)-C(5B)	1.534(3)

C(5B)-C(6B)	1.536(3)
C(6B)-C(7B)	1.523(3)
C(6B)-C(15B)	1.533(3)
C(8B)-C(9B)	1.517(3)
C(9B)-C(10B)	1.528(3)
C(10B)-C(11B)	1.531(3)
C(11B)-C(12B)	1.532(3)
C(12B)-C(13B)	1.522(3)
C(13B)-C(14B)	1.526(3)
C(13B)-C(15B)	1.532(3)
C(16B)-C(23B)	1.512(3)
C(16B)-C(17B)	1.523(3)
C(17B)-C(22B)	1.388(3)
C(17B)-C(18B)	1.391(3)
C(18B)-C(19B)	1.394(3)
C(19B)-C(20B)	1.388(3)
C(20B)-C(21B)	1.379(3)
C(21B)-C(22B)	1.392(3)
Cl(1)-C(1)	1.766(2)
Cl(2)-C(1)	1.771(2)
Cl(3)-C(2)	1.758(2)
Cl(4)-C(2)	1.780(2)
Cl(5)-C(3)	1.752(2)
Cl(6)-C(3)	1.756(2)
Cl(7)-C(4)	1.776(3)
Cl(8)-C(4)	1.752(3)

O(1A)-Pd(1)-N(2A)	176.27(6)
O(1A)-Pd(1)-N(1A)	89.78(6)
N(2A)-Pd(1)-N(1A)	88.07(6)
O(1A)-Pd(1)-Cl(1A)	87.71(4)
N(2A)-Pd(1)-Cl(1A)	95.16(4)
N(1A)-Pd(1)-Cl(1A)	164.59(5)
C(16A)-O(1A)-Pd(1)	116.60(12)
C(14A)-N(1A)-C(1A)	109.38(15)
C(14A)-N(1A)-C(5A)	112.71(15)
C(1A)-N(1A)-C(5A)	109.47(15)
C(14A)-N(1A)-Pd(1)	111.32(12)
C(1A)-N(1A)-Pd(1)	109.42(12)
C(5A)-N(1A)-Pd(1)	104.43(11)
C(7A)-N(2A)-C(8A)	107.75(14)
C(7A)-N(2A)-C(12A)	111.01(14)
C(8A)-N(2A)-C(12A)	106.35(15)
C(7A)-N(2A)-Pd(1)	105.65(11)
C(8A)-N(2A)-Pd(1)	114.91(11)
C(12A)-N(2A)-Pd(1)	111.18(11)
N(1A)-C(1A)-C(2A)	114.37(17)
C(1A)-C(2A)-C(3A)	109.16(17)
C(4A)-C(3A)-C(2A)	108.86(18)
C(3A)-C(4A)-C(5A)	114.05(18)
N(1A)-C(5A)-C(4A)	114.01(16)
N(1A)-C(5A)-C(6A)	110.60(16)
C(4A)-C(5A)-C(6A)	110.21(16)
C(7A)-C(6A)-C(15A)	108.46(17)
C(7A)-C(6A)-C(5A)	115.59(16)
C(15A)-C(6A)-C(5A)	110.57(16)
N(2A)-C(7A)-C(6A)	113.05(16)
N(2A)-C(8A)-C(9A)	113.46(16)
C(8A)-C(9A)-C(10A)	112.24(17)
C(11A)-C(10A)-C(9A)	109.49(17)
C(10A)-C(11A)-C(12A)	110.33(16)
N(2A)-C(12A)-C(13A)	112.53(16)
N(2A)-C(12A)-C(11A)	109.26(15)
C(13A)-C(12A)-C(11A)	115.21(16)
C(14A)-C(13A)-C(12A)	115.02(16)
C(14A)-C(13A)-C(15A)	109.37(17)
C(12A)-C(13A)-C(15A)	109.23(16)
N(1A)-C(14A)-C(13A)	112.92(16)
C(13A)-C(15A)-C(6A)	106.51(15)
O(1A)-C(16A)-C(23A)	105.17(16)
O(1A)-C(16A)-C(17A)	115.29(16)
C(23A)-C(16A)-C(17A)	111.31(17)
C(22A)-C(17A)-C(18A)	117.9(2)
C(22A)-C(17A)-C(16A)	120.47(19)
C(18A)-C(17A)-C(16A)	121.62(19)
C(19A)-C(18A)-C(17A)	121.2(2)
C(18A)-C(19A)-C(20A)	119.3(2)
C(21A)-C(20A)-C(19A)	120.3(2)
C(20A)-C(21A)-C(22A)	119.4(2)
C(21A)-C(22A)-C(17A)	121.8(2)
F(2A)-C(23A)-F(1A)	106.42(17)
F(2A)-C(23A)-F(3A)	106.08(17)
F(1A)-C(23A)-F(3A)	105.72(18)
F(2A)-C(23A)-C(16A)	112.35(18)
F(1A)-C(23A)-C(16A)	112.28(17)
F(3A)-C(23A)-C(16A)	113.43(17)
O(1B)-Pd(2)-N(2B)	174.13(6)
O(1B)-Pd(2)-N(1B)	90.94(6)
N(2B)-Pd(2)-N(1B)	87.58(6)
O(1B)-Pd(2)-Cl(1B)	87.82(4)
N(2B)-Pd(2)-Cl(1B)	95.24(5)
N(1B)-Pd(2)-Cl(1B)	163.00(5)
C(16B)-O(1B)-Pd(2)	114.46(12)
C(14B)-N(1B)-C(1B)	109.72(15)
C(14B)-N(1B)-C(5B)	112.21(15)
C(1B)-N(1B)-C(5B)	109.15(15)
C(14B)-N(1B)-Pd(2)	111.73(12)
C(1B)-N(1B)-Pd(2)	108.59(12)
C(5B)-N(1B)-Pd(2)	105.29(11)
C(7B)-N(2B)-C(8B)	108.17(15)
C(7B)-N(2B)-C(12B)	110.69(15)
C(8B)-N(2B)-C(12B)	106.13(16)
C(7B)-N(2B)-Pd(2)	106.80(12)
C(8B)-N(2B)-Pd(2)	114.37(12)
C(12B)-N(2B)-Pd(2)	110.70(12)
N(1B)-C(1B)-C(2B)	114.80(16)
C(3B)-C(2B)-C(1B)	110.19(17)
C(2B)-C(3B)-C(4B)	108.64(18)
C(3B)-C(4B)-C(5B)	114.21(17)
N(1B)-C(5B)-C(4B)	113.38(16)
N(1B)-C(5B)-C(6B)	110.94(17)
C(4B)-C(5B)-C(6B)	109.68(17)
C(7B)-C(6B)-C(15B)	108.63(18)
C(7B)-C(6B)-C(5B)	115.20(17)
C(15B)-C(6B)-C(5B)	110.31(17)
N(2B)-C(7B)-C(6B)	113.25(16)

N(2B)-C(8B)-C(9B)	113.50(16)	C(18B)-C(17B)-C(16B)	120.55(19)
C(8B)-C(9B)-C(10B)	112.23(18)	C(17B)-C(18B)-C(19B)	120.6(2)
C(9B)-C(10B)-C(11B)	109.21(18)	C(20B)-C(19B)-C(18B)	120.0(2)
C(10B)-C(11B)-C(12B)	109.94(17)	C(21B)-C(20B)-C(19B)	119.8(2)
N(2B)-C(12B)-C(13B)	112.69(17)	C(20B)-C(21B)-C(22B)	119.9(2)
N(2B)-C(12B)-C(11B)	109.69(16)	C(17B)-C(22B)-C(21B)	121.1(2)
C(13B)-C(12B)-C(11B)	114.75(17)	F(3B)-C(23B)-F(2B)	106.45(17)
C(12B)-C(13B)-C(14B)	115.49(17)	F(3B)-C(23B)-F(1B)	105.80(19)
C(12B)-C(13B)-C(15B)	108.85(17)	F(2B)-C(23B)-F(1B)	106.22(17)
C(14B)-C(13B)-C(15B)	109.29(18)	F(3B)-C(23B)-C(16B)	113.32(17)
N(1B)-C(14B)-C(13B)	112.61(16)	F(2B)-C(23B)-C(16B)	112.11(19)
C(13B)-C(15B)-C(6B)	106.30(16)	F(1B)-C(23B)-C(16B)	112.42(17)
O(1B)-C(16B)-C(23B)	106.98(18)	Cl(1)-C(1)-Cl(2)	112.06(13)
O(1B)-C(16B)-C(17B)	114.46(16)	Cl(3)-C(2)-Cl(4)	111.44(13)
C(23B)-C(16B)-C(17B)	111.21(17)	Cl(5)-C(3)-Cl(6)	112.04(12)
C(22B)-C(17B)-C(18B)	118.5(2)	Cl(8)-C(4)-Cl(7)	112.80(15)
C(22B)-C(17B)-C(16B)	120.97(19)		

X-ray crystallographic structure for **[(sparteine)Pd(*R*-OCH(CF_3)C_6H_5)$_2$ (33)**. The crystallographic data for **33** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 260858.

Crystal data and structural refinement for 33 (CCDC 260858).

Empirical formula	$C_{31}H_{38}F_6N_2O_2Pd \bullet CH_2Cl_2$
Formula weight	775.96
Crystallization solvent	Dichloromethane/hexane
Crystal habit	Prism
Crystal size	0.44 x 0.29 x 0.09 mm^3
Crystal color	Yellow
Data collection	
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 17094 reflections used in lattice determination	2.30 to 41.38°
Unit cell dimensions	a = 10.7694(4) Å b = 13.1518(5) Å β = 105.6820(10)° c = 11.4564(4) Å
Volume	1562.25(10) $Å^3$
Z	2
Crystal system	Monoclinic
Space group	$P2_1$
Density (calculated)	1.650 Mg/m^3
F(000)	792
Data collection program	Bruker SMART v5.630
θ range for data collection	1.85 to 42.67°
Completeness to θ = 42.67°	91.7 %
Index ranges	$-18 \le h \le 20$, $-24 \le k \le 24$, $-20 \le l \le 21$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	31764
Independent reflections	17119 [R_{int}= 0.0618]
Absorption coefficient	0.835 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9286 and 0.7102
Structure solution and refinement	
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	17119 / 1 / 566
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.067
Final R indices [I>2σ(I), 14299 reflections]	R1 = 0.0375, *w*R2 = 0.0708
R indices (all data)	R1 = 0.0489, *w*R2 = 0.0733
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	-0.049(12)
Largest diff. peak and hole	2.146 and -1.876 e.$Å^{-3}$

Special refinement details

All difference Fourier peaks larger than 1e/Å^3 lie with 1Å of Pd.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

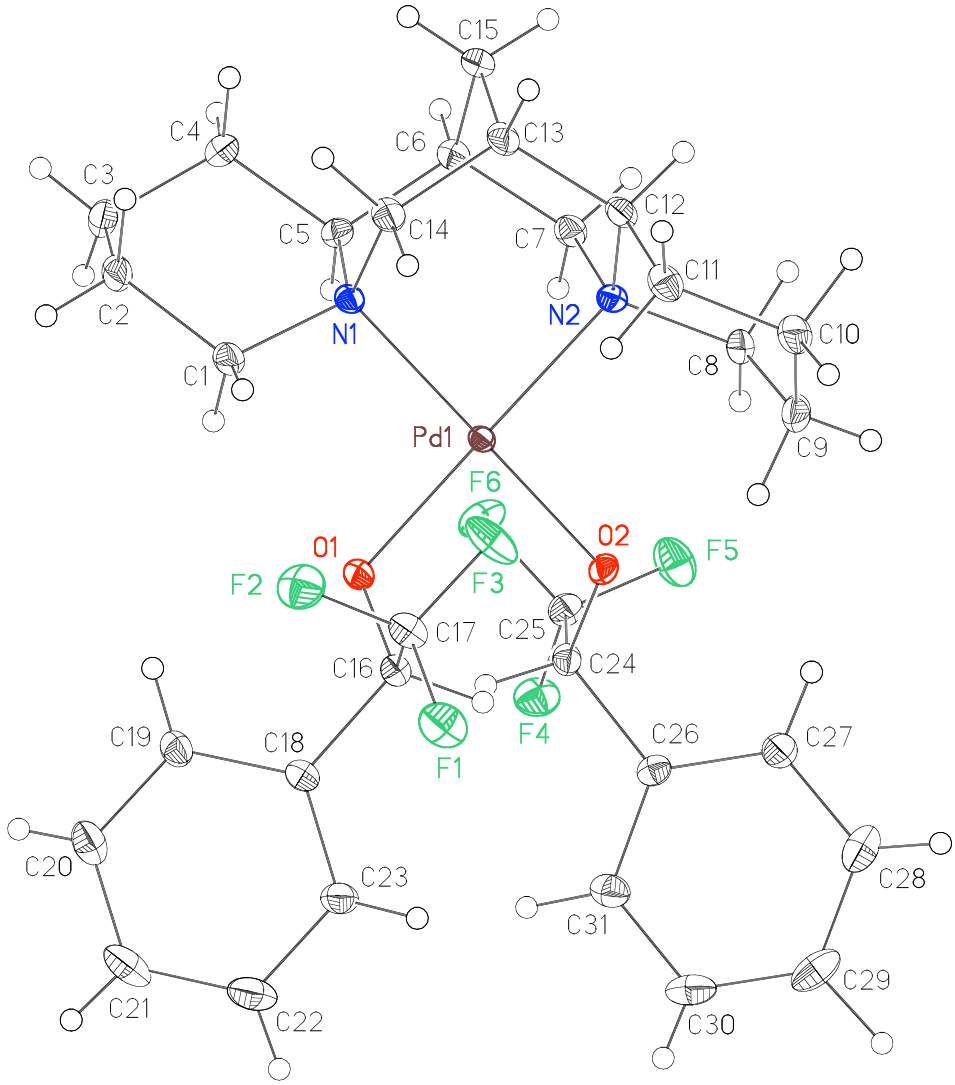

Figure S16. Molecule of **33**.

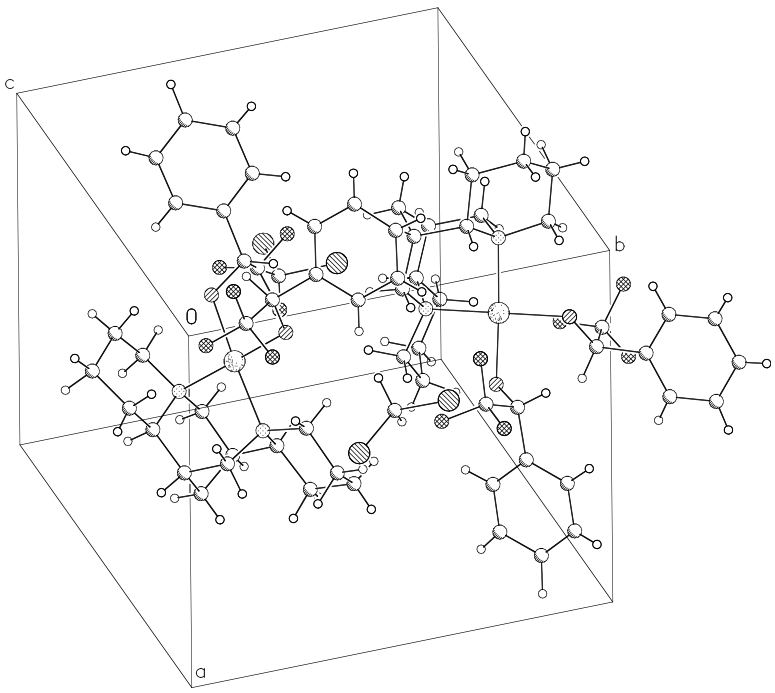

Figure S17. Unit cell contents of **33**.

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **33** (CCDC 259858). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	6173(1)	3730(1)	6585(1)	9(1)
F(1)	7204(2)	5258(1)	10414(1)	24(1)
F(2)	8293(1)	5661(1)	9148(1)	24(1)
F(3)	7651(2)	4119(1)	9227(1)	27(1)
F(4)	1711(1)	4422(1)	5130(1)	20(1)
F(5)	2404(2)	2875(1)	5293(1)	24(1)
F(6)	3481(1)	4050(1)	4690(1)	22(1)
O(1)	6101(1)	5181(1)	7153(1)	13(1)
O(2)	4605(1)	3427(1)	7153(1)	13(1)
N(1)	7672(2)	4063(1)	5776(2)	11(1)
N(2)	6308(2)	2206(1)	6075(2)	11(1)
C(1)	8007(2)	5173(1)	5972(2)	15(1)
C(2)	8859(2)	5592(2)	5215(2)	19(1)
C(3)	8199(2)	5445(2)	3872(2)	19(1)
C(4)	7924(2)	4314(2)	3639(2)	18(1)
C(5)	7123(2)	3853(2)	4436(2)	13(1)
C(6)	6947(2)	2701(1)	4187(2)	14(1)
C(7)	5941(2)	2200(2)	4720(2)	13(1)
C(8)	5382(2)	1510(1)	6469(2)	15(1)
C(9)	5682(2)	1410(2)	7839(2)	17(1)
C(10)	7073(2)	1092(2)	8415(2)	17(1)
C(11)	7990(2)	1783(2)	7968(2)	16(1)
C(12)	7645(2)	1781(1)	6585(2)	14(1)
C(13)	8628(2)	2300(2)	6045(2)	16(1)
C(14)	8841(2)	3437(1)	6327(2)	15(1)
C(15)	8235(2)	2142(2)	4679(2)	17(1)
C(16)	6021(2)	5339(1)	8326(2)	13(1)

C(17)	7287(2)	5093(2)	9274(2)	17(1)
C(18)	5683(2)	6447(1)	8494(2)	13(1)
C(19)	6216(2)	7219(2)	7942(2)	15(1)
C(20)	5973(2)	8235(2)	8129(2)	20(1)
C(21)	5186(3)	8495(2)	8870(2)	24(1)
C(22)	4620(2)	7737(2)	9398(2)	23(1)
C(23)	4873(2)	6713(2)	9209(2)	17(1)
C(24)	3556(2)	4067(1)	6804(2)	12(1)
C(25)	2789(2)	3851(2)	5487(2)	14(1)
C(26)	2669(2)	3929(1)	7636(2)	12(1)
C(27)	2502(2)	2962(2)	8065(2)	16(1)
C(28)	1707(2)	2810(2)	8821(2)	21(1)
C(29)	1073(2)	3651(3)	9166(2)	22(1)
C(30)	1255(2)	4611(2)	8757(2)	20(1)
C(31)	2045(2)	4754(2)	7991(2)	17(1)
Cl(1)	396(1)	4352(1)	2045(1)	38(1)
Cl(2)	-966(1)	2414(1)	1556(1)	41(1)
C(41)	524(4)	3018(3)	2170(4)	37(1)

Table S10. Bond lengths [Å] and angles [°] for **33** (CCDC 259858).

Pd(1)-O(2)	2.0070(13)	C(7)-H(7A)	0.99(3)
Pd(1)-O(1)	2.0237(13)	C(7)-H(7B)	0.92(3)
Pd(1)-N(2)	2.1042(16)	C(8)-C(9)	1.521(3)
Pd(1)-N(1)	2.1127(15)	C(8)-H(8A)	1.01(3)
F(1)-C(17)	1.351(2)	C(8)-H(8B)	1.00(3)
F(2)-C(17)	1.356(3)	C(9)-C(10)	1.523(3)
F(3)-C(17)	1.345(2)	C(9)-H(9A)	0.86(4)
F(4)-C(25)	1.349(2)	C(9)-H(9B)	0.99(3)
F(5)-C(25)	1.348(3)	C(10)-C(11)	1.529(3)
F(6)-C(25)	1.351(2)	C(10)-H(10A)	1.02(3)
O(1)-C(16)	1.385(2)	C(10)-H(10B)	0.97(3)
O(2)-C(24)	1.379(2)	C(11)-C(12)	1.526(3)
N(1)-C(14)	1.494(2)	C(11)-H(11A)	0.95(3)
N(1)-C(1)	1.506(2)	C(11)-H(11B)	0.84(3)
N(1)-C(5)	1.514(2)	C(12)-C(13)	1.525(3)
N(2)-C(7)	1.495(3)	C(12)-H(12)	0.96(3)
N(2)-C(12)	1.507(3)	C(13)-C(15)	1.521(3)
N(2)-C(8)	1.510(2)	C(13)-C(14)	1.533(3)
C(1)-C(2)	1.526(3)	C(13)-H(13)	0.96(4)
C(1)-H(1A)	0.82(2)	C(14)-H(14A)	0.94(2)
C(1)-H(1B)	1.00(3)	C(14)-H(14B)	0.96(2)
C(2)-C(3)	1.522(4)	C(15)-H(15A)	0.92(4)
C(2)-H(2A)	0.93(3)	C(15)-H(15B)	0.91(3)
C(2)-H(2B)	1.10(3)	C(16)-C(18)	1.526(3)
C(3)-C(4)	1.526(3)	C(16)-C(17)	1.531(3)
C(3)-H(3A)	0.87(3)	C(16)-H(16)	1.01(2)
C(3)-H(3B)	0.89(3)	C(18)-C(23)	1.393(3)
C(4)-C(5)	1.540(3)	C(18)-C(19)	1.399(3)
C(4)-H(4A)	0.98(2)	C(19)-C(20)	1.390(3)
C(4)-H(4B)	0.91(3)	C(19)-H(19)	0.91(3)
C(5)-C(6)	1.544(3)	C(20)-C(21)	1.395(4)
C(5)-H(5)	0.97(3)	C(20)-H(20)	0.78(3)
C(6)-C(7)	1.529(3)	C(21)-C(22)	1.390(4)
C(6)-C(15)	1.537(3)	C(21)-H(21)	0.85(3)
C(6)-H(6)	1.04(2)	C(22)-C(23)	1.403(3)

C(22)-H(22)	0.87(3)
C(23)-H(23)	0.89(3)
C(24)-C(26)	1.532(2)
C(24)-C(25)	1.539(3)
C(24)-H(24)	0.93(3)
C(26)-C(27)	1.393(3)
C(26)-C(31)	1.394(3)
C(27)-C(28)	1.388(3)
C(27)-H(27)	0.92(3)
C(28)-C(29)	1.410(4)
C(28)-H(28)	0.88(3)
C(29)-C(30)	1.379(4)
C(29)-H(29)	1.08(2)
C(30)-C(31)	1.390(3)
C(30)-H(30)	0.82(4)
C(31)-H(31)	0.95(3)
Cl(1)-C(41)	1.762(4)
Cl(2)-C(41)	1.757(4)
C(41)-H(41A)	1.02(4)
C(41)-H(41B)	1.02(3)

O(2)-Pd(1)-O(1)	88.53(5)
O(2)-Pd(1)-N(2)	91.57(6)
O(1)-Pd(1)-N(2)	177.26(7)
O(2)-Pd(1)-N(1)	173.14(6)
O(1)-Pd(1)-N(1)	92.65(6)
N(2)-Pd(1)-N(1)	87.57(6)
C(16)-O(1)-Pd(1)	118.15(11)
C(24)-O(2)-Pd(1)	118.66(11)
C(14)-N(1)-C(1)	109.32(15)
C(14)-N(1)-C(5)	112.41(15)
C(1)-N(1)-C(5)	109.92(15)
C(14)-N(1)-Pd(1)	110.89(12)
C(1)-N(1)-Pd(1)	108.44(11)
C(5)-N(1)-Pd(1)	105.74(10)
C(7)-N(2)-C(12)	110.92(14)
C(7)-N(2)-C(8)	107.21(15)
C(12)-N(2)-C(8)	107.35(14)
C(7)-N(2)-Pd(1)	105.93(11)
C(12)-N(2)-Pd(1)	112.12(11)
C(8)-N(2)-Pd(1)	113.23(11)
N(1)-C(1)-C(2)	114.95(16)
N(1)-C(1)-H(1A)	103.4(16)
C(2)-C(1)-H(1A)	114.7(17)
N(1)-C(1)-H(1B)	105.1(15)
C(2)-C(1)-H(1B)	105.1(15)
H(1A)-C(1)-H(1B)	113(2)
C(3)-C(2)-C(1)	109.91(18)
C(3)-C(2)-H(2A)	111.8(18)
C(1)-C(2)-H(2A)	110.1(18)
C(3)-C(2)-H(2B)	110.4(16)
C(1)-C(2)-H(2B)	111.3(16)
H(2A)-C(2)-H(2B)	103(2)
C(2)-C(3)-C(4)	108.44(18)
C(2)-C(3)-H(3A)	111(2)
C(4)-C(3)-H(3A)	110(2)
C(2)-C(3)-H(3B)	112.2(19)
C(4)-C(3)-H(3B)	112(2)
H(3A)-C(3)-H(3B)	102(3)
C(3)-C(4)-C(5)	113.16(17)
C(3)-C(4)-H(4A)	108.8(13)
C(5)-C(4)-H(4A)	111.1(13)
C(3)-C(4)-H(4B)	111.8(17)
C(5)-C(4)-H(4B)	111.4(18)
H(4A)-C(4)-H(4B)	100(2)
N(1)-C(5)-C(4)	113.66(16)
N(1)-C(5)-C(6)	111.23(15)
C(4)-C(5)-C(6)	109.65(15)
N(1)-C(5)-H(5)	111.7(19)
C(4)-C(5)-H(5)	105.3(18)
C(6)-C(5)-H(5)	104.7(18)
C(7)-C(6)-C(15)	108.29(16)
C(7)-C(6)-C(5)	114.43(15)
C(15)-C(6)-C(5)	110.38(16)
C(7)-C(6)-H(6)	104.2(14)
C(15)-C(6)-H(6)	111.0(14)
C(5)-C(6)-H(6)	108.3(13)
N(2)-C(7)-C(6)	113.30(16)
N(2)-C(7)-H(7A)	111.0(14)
C(6)-C(7)-H(7A)	109.6(14)
N(2)-C(7)-H(7B)	111.4(18)
C(6)-C(7)-H(7B)	107.8(17)
H(7A)-C(7)-H(7B)	103(2)
N(2)-C(8)-C(9)	112.77(16)
N(2)-C(8)-H(8A)	104.1(15)
C(9)-C(8)-H(8A)	114.1(15)
N(2)-C(8)-H(8B)	110.5(15)
C(9)-C(8)-H(8B)	110.9(15)
H(8A)-C(8)-H(8B)	104(2)
C(8)-C(9)-C(10)	112.38(17)
C(8)-C(9)-H(9A)	121(3)
C(10)-C(9)-H(9A)	103(3)
C(8)-C(9)-H(9B)	113.2(15)
C(10)-C(9)-H(9B)	110.4(16)
H(9A)-C(9)-H(9B)	95(3)
C(9)-C(10)-C(11)	109.95(17)
C(9)-C(10)-H(10A)	114.8(17)
C(11)-C(10)-H(10A)	105.0(16)
C(9)-C(10)-H(10B)	114.8(19)
C(11)-C(10)-H(10B)	112.5(19)
H(10A)-C(10)-H(10B)	99(2)
C(12)-C(11)-C(10)	110.37(17)
C(12)-C(11)-H(11A)	112.9(19)
C(10)-C(11)-H(11A)	109.5(19)
C(12)-C(11)-H(11B)	104.9(19)
C(10)-C(11)-H(11B)	113.5(19)
H(11A)-C(11)-H(11B)	106(3)
N(2)-C(12)-C(13)	111.80(16)
N(2)-C(12)-C(11)	109.93(15)
C(13)-C(12)-C(11)	114.81(17)
N(2)-C(12)-H(12)	107.5(17)
C(13)-C(12)-H(12)	105.2(17)
C(11)-C(12)-H(12)	107.2(16)
C(15)-C(13)-C(12)	109.04(17)
C(15)-C(13)-C(14)	109.53(17)
C(12)-C(13)-C(14)	115.59(16)

C(15)-C(13)-H(13)	113(2)	C(23)-C(22)-H(22)	117.7(19)
C(12)-C(13)-H(13)	99(2)	C(18)-C(23)-C(22)	120.7(2)
C(14)-C(13)-H(13)	110(2)	C(18)-C(23)-H(23)	121(2)
N(1)-C(14)-C(13)	112.81(16)	C(22)-C(23)-H(23)	117(2)
N(1)-C(14)-H(14A)	106.3(15)	O(2)-C(24)-C(26)	110.30(15)
C(13)-C(14)-H(14A)	108.2(14)	O(2)-C(24)-C(25)	110.57(16)
N(1)-C(14)-H(14B)	109.4(16)	C(26)-C(24)-C(25)	109.17(15)
C(13)-C(14)-H(14B)	107.6(18)	O(2)-C(24)-H(24)	113.6(16)
H(14A)-C(14)-H(14B)	113(2)	C(26)-C(24)-H(24)	110.0(15)
C(13)-C(15)-C(6)	106.53(16)	C(25)-C(24)-H(24)	103.0(16)
C(13)-C(15)-H(15A)	108(2)	F(5)-C(25)-F(4)	106.17(17)
C(6)-C(15)-H(15A)	109(2)	F(5)-C(25)-F(6)	105.99(16)
C(13)-C(15)-H(15B)	113(2)	F(4)-C(25)-F(6)	105.85(16)
C(6)-C(15)-H(15B)	106(2)	F(5)-C(25)-C(24)	113.42(16)
H(15A)-C(15)-H(15B)	115(3)	F(4)-C(25)-C(24)	112.59(17)
O(1)-C(16)-C(18)	110.21(16)	F(6)-C(25)-C(24)	112.23(16)
O(1)-C(16)-C(17)	112.30(16)	C(27)-C(26)-C(31)	119.33(17)
C(18)-C(16)-C(17)	108.03(16)	C(27)-C(26)-C(24)	119.33(16)
O(1)-C(16)-H(16)	117.8(13)	C(31)-C(26)-C(24)	121.33(16)
C(18)-C(16)-H(16)	111.1(13)	C(28)-C(27)-C(26)	120.76(19)
C(17)-C(16)-H(16)	96.3(14)	C(28)-C(27)-H(27)	117.8(19)
F(3)-C(17)-F(1)	106.73(17)	C(26)-C(27)-H(27)	121.5(19)
F(3)-C(17)-F(2)	105.74(17)	C(27)-C(28)-C(29)	119.3(2)
F(1)-C(17)-F(2)	106.15(17)	C(27)-C(28)-H(28)	125(2)
F(3)-C(17)-C(16)	112.75(17)	C(29)-C(28)-H(28)	115(2)
F(1)-C(17)-C(16)	111.89(17)	C(30)-C(29)-C(28)	119.91(19)
F(2)-C(17)-C(16)	113.07(17)	C(30)-C(29)-H(29)	121.6(13)
C(23)-C(18)-C(19)	118.84(18)	C(28)-C(29)-H(29)	117.5(13)
C(23)-C(18)-C(16)	121.50(17)	C(29)-C(30)-C(31)	120.4(2)
C(19)-C(18)-C(16)	119.65(17)	C(29)-C(30)-H(30)	122(3)
C(20)-C(19)-C(18)	120.72(19)	C(31)-C(30)-H(30)	117(3)
C(20)-C(19)-H(19)	120.8(16)	C(30)-C(31)-C(26)	120.3(2)
C(18)-C(19)-H(19)	118.5(16)	C(30)-C(31)-H(31)	118.0(15)
C(19)-C(20)-C(21)	120.0(2)	C(26)-C(31)-H(31)	121.4(15)
C(19)-C(20)-H(20)	121(2)	Cl(2)-C(41)-Cl(1)	112.0(2)
C(21)-C(20)-H(20)	118(2)	Cl(2)-C(41)-H(41A)	109(2)
C(22)-C(21)-C(20)	119.9(2)	Cl(1)-C(41)-H(41A)	109(2)
C(22)-C(21)-H(21)	123(2)	Cl(2)-C(41)-H(41B)	108.8(19)
C(20)-C(21)-H(21)	117(2)	Cl(1)-C(41)-H(41B)	102(2)
C(21)-C(22)-C(23)	119.7(2)	H(41A)-C(41)-H(41B)	115(3)
C(21)-C(22)-H(22)	122.1(19)		

X-ray crystallographic structure for **[(sparteine)PdBr$_2$ (45)**. The crystallographic data for **45** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 298214.

Crystal data and structure refinement for 45 (CCDC 298214).

Empirical formula	$C_{15}H_{26}N_2Br_2Pd \bullet CH_2Cl_2$
Formula weight	585.52
Crystallization solvent	Dichloromethane/pentane
Crystal habit	Blade
Crystal size	0.31 x 0.18 x 0.10 mm^3
Crystal color	Dark red
Data collection	
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 19178 reflections used in lattice determination	2.64 to 37.85°
Unit cell dimensions	a = 8.8518(3) Å b = 14.7348(4) Å c = 15.4442(4) Å
Volume	2014.38(10) Å^3
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.931 Mg/m^3
F(000)	1152
Data collection program	Bruker SMART v5.630
θ range for data collection	1.91 to 38.18°
Completeness to θ = 38.18°	98.0 %
Index ranges	$-15 \le h \le 15$, $-25 \le k \le 25$, $-26 \le l \le 26$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	52177
Independent reflections	10756 [R_{int}= 0.0625]
Absorption coefficient	5.154 mm^{-1}
Absorption correction	SADABS
Max. and min. transmission	1.000000 and 0.647147
Structure solution and refinement.	
Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	10756 / 0 / 208
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.046
Final R indices [I>2σ(I), 8371 reflections]	R1 = 0.0341, *w*R2 = 0.0526
R indices (all data)	R1 = 0.0565, *w*R2 = 0.0574
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure determination	Anomalous dispersion
Absolute structure parameter	0.011(4)
Largest diff. peak and hole	1.149 and -0.876 e.Å^{-3}

Special refinement details.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

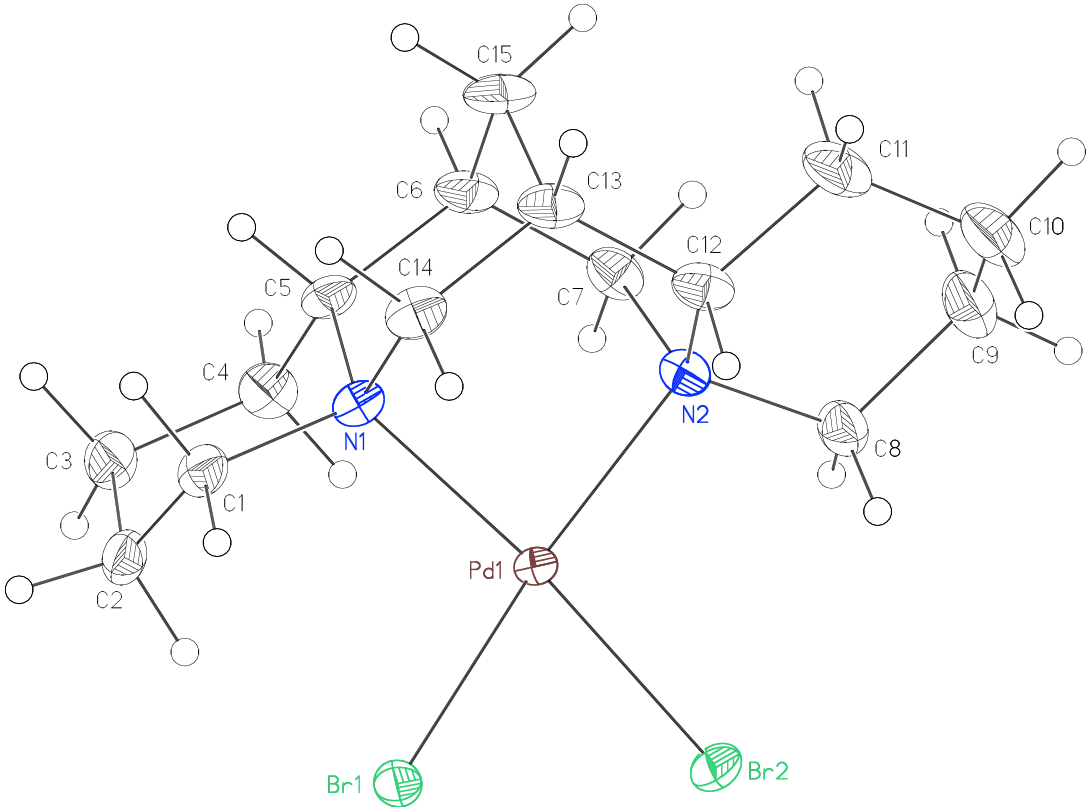

Figure S18. Molecule of **45**. Atom numbering differs from that shown in Scheme 9.

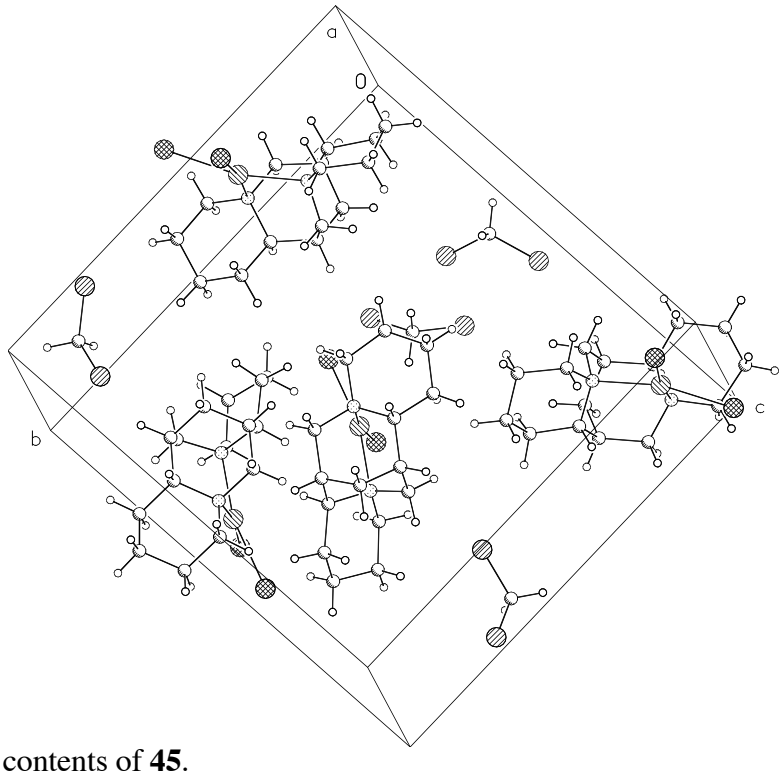

Figure S19. Unit cell contents of **45**.

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **45** (CCDC 259214). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	3767(1)	1058(1)	9264(1)	13(1)
Br(1)	3925(1)	416(1)	10723(1)	23(1)
Br(2)	6528(1)	893(1)	9277(1)	24(1)
N(1)	1379(2)	984(1)	9210(1)	16(1)
N(2)	3661(2)	1931(1)	8150(1)	18(1)
C(1)	644(3)	382(2)	9876(2)	21(1)
C(2)	1012(3)	-618(2)	9760(2)	22(1)
C(3)	669(3)	-955(2)	8852(2)	26(1)
C(4)	1390(3)	-325(2)	8194(2)	23(1)
C(5)	844(3)	641(2)	8333(1)	20(1)
C(6)	1191(3)	1302(2)	7603(2)	23(1)
C(7)	2865(3)	1470(2)	7423(2)	21(1)
C(8)	5230(3)	2193(2)	7861(2)	24(1)
C(9)	5307(3)	2964(2)	7200(2)	32(1)
C(10)	4599(4)	3813(2)	7582(2)	35(1)
C(11)	2979(3)	3591(2)	7839(2)	32(1)
C(12)	2831(3)	2778(2)	8455(2)	22(1)
C(13)	1155(3)	2579(2)	8624(2)	24(1)
C(14)	831(2)	1933(2)	9368(2)	22(1)
C(15)	410(3)	2204(2)	7805(2)	28(1)
C(20)	8408(3)	1359(2)	5322(2)	36(1)
Cl(1)	7393(1)	2244(1)	4808(1)	38(1)
Cl(2)	7559(1)	1047(1)	6310(1)	36(1)

Table S12. Bond lengths [Å] and angles [°] for **45**. (CCDC 298214).

Pd(1)-N(1)	2.1184(16)	C(1)-N(1)-C(5)	106.14(17)
Pd(1)-N(2)	2.1510(18)	C(14)-N(1)-Pd(1)	105.53(13)
Pd(1)-Br(1)	2.4474(3)	C(1)-N(1)-Pd(1)	115.73(13)
Pd(1)-Br(2)	2.4560(3)	C(5)-N(1)-Pd(1)	111.30(13)
N(1)-C(14)	1.501(3)	C(7)-N(2)-C(8)	109.20(18)
N(1)-C(1)	1.506(3)	C(7)-N(2)-C(12)	112.30(18)
N(1)-C(5)	1.520(3)	C(8)-N(2)-C(12)	109.03(18)
N(2)-C(7)	1.490(3)	C(7)-N(2)-Pd(1)	110.53(14)
N(2)-C(8)	1.509(3)	C(8)-N(2)-Pd(1)	110.43(14)
N(2)-C(12)	1.522(3)	C(12)-N(2)-Pd(1)	105.30(14)
C(1)-C(2)	1.519(4)	N(1)-C(1)-C(2)	113.45(19)
C(2)-C(3)	1.518(3)	C(1)-C(2)-C(3)	112.5(2)
C(3)-C(4)	1.517(4)	C(4)-C(3)-C(2)	109.52(19)
C(4)-C(5)	1.518(3)	C(3)-C(4)-C(5)	110.2(2)
C(5)-C(6)	1.522(3)	C(6)-C(5)-N(1)	112.60(18)
C(6)-C(7)	1.528(4)	C(6)-C(5)-C(4)	115.5(2)
C(6)-C(15)	1.531(3)	N(1)-C(5)-C(4)	109.79(18)
C(8)-C(9)	1.529(4)	C(5)-C(6)-C(7)	115.74(19)
C(9)-C(10)	1.518(4)	C(5)-C(6)-C(15)	108.3(2)
C(10)-C(11)	1.524(4)	C(7)-C(6)-C(15)	109.6(2)
C(11)-C(12)	1.536(4)	N(2)-C(7)-C(6)	113.26(19)
C(12)-C(13)	1.535(4)	N(2)-C(8)-C(9)	115.4(2)
C(13)-C(14)	1.519(4)	C(10)-C(9)-C(8)	109.5(2)
C(13)-C(15)	1.530(4)	C(9)-C(10)-C(11)	108.2(2)
C(20)-Cl(2)	1.761(3)	C(10)-C(11)-C(12)	114.1(2)
C(20)-Cl(1)	1.771(3)	N(2)-C(12)-C(11)	114.0(2)
		N(2)-C(12)-C(13)	111.27(19)
N(1)-Pd(1)-N(2)	87.43(7)	C(11)-C(12)-C(13)	109.6(2)
N(1)-Pd(1)-Br(1)	94.22(5)	C(14)-C(13)-C(15)	108.6(2)
N(2)-Pd(1)-Br(1)	165.96(5)	C(14)-C(13)-C(12)	115.46(19)
N(1)-Pd(1)-Br(2)	171.20(5)	C(15)-C(13)-C(12)	110.2(2)
N(2)-Pd(1)-Br(2)	96.25(5)	N(1)-C(14)-C(13)	113.54(19)
Br(1)-Pd(1)-Br(2)	84.155(10)	C(13)-C(15)-C(6)	106.70(19)
C(14)-N(1)-C(1)	107.33(18)	Cl(2)-C(20)-Cl(1)	111.38(16)
C(14)-N(1)-C(5)	110.77(18)		

X-ray crystallographic structure for **[(α-isosparteine)$PdCl_2$ (49)**. The crystallographic data for **49** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 223628.

Crystal data and structure refinement for 49 (CCDC 223628).

Empirical formula	$C_{15}H_{26}Cl_2N_2Pd$
Formula weight	411.68
Crystallization solvent	Dichloromethane
Crystal habit	Fragment
Crystal size	0.39 x 0.24 x 0.22 mm^3
Crystal color	Maroon
Data collection	
Preliminary photos	Rotation
Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data collection temperature	100(2) K
θ range for 24049 reflections used in lattice determination	2.22 to 44.96°
Unit cell dimensions	a = 9.2815(3) Å b = 11.4873(4) Å c = 15.1073(5) Å
Volume	1610.73(9) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.698 Mg/m^3
F(000)	840
Data collection program	Bruker SMART v5.054
θ range for data collection	2.23 to 44.97°
Completeness to θ = 44.97°	94.4 %
Index ranges	$-17 \le h \le 16$, $-22 \le k \le 20$, $-28 \le l \le 29$
Data collection scan type	ω scans at 7 ϕ settings
Data reduction program	Bruker SAINT v6.45
Reflections collected	44470
Independent reflections	11830 [R_{int}= 0.0673]
Absorption coefficient	1.476 mm^{-1}
Absorption correction	None
Max. and min. transmission (predicted)	0.7372 and 0.5968
Structure solution and refinement	
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Difference Fourier map
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11830 / 0 / 285
Treatment of hydrogen atoms	Unrestrained
Goodness-of-fit on F^2	1.139
Final R indices [$I>2\sigma(I)$, 9732 reflections]	R1 = 0.0317, *w*R2 = 0.0525
R indices (all data)	R1 = 0.0452, *w*R2 = 0.0542
Type of weighting scheme used	Sigma
Weighting scheme used	$w = 1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Absolute structure parameter	-0.042(13)
Largest diff. peak and hole	1.557 and -1.497 e.$Å^3$

Special refinement details.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

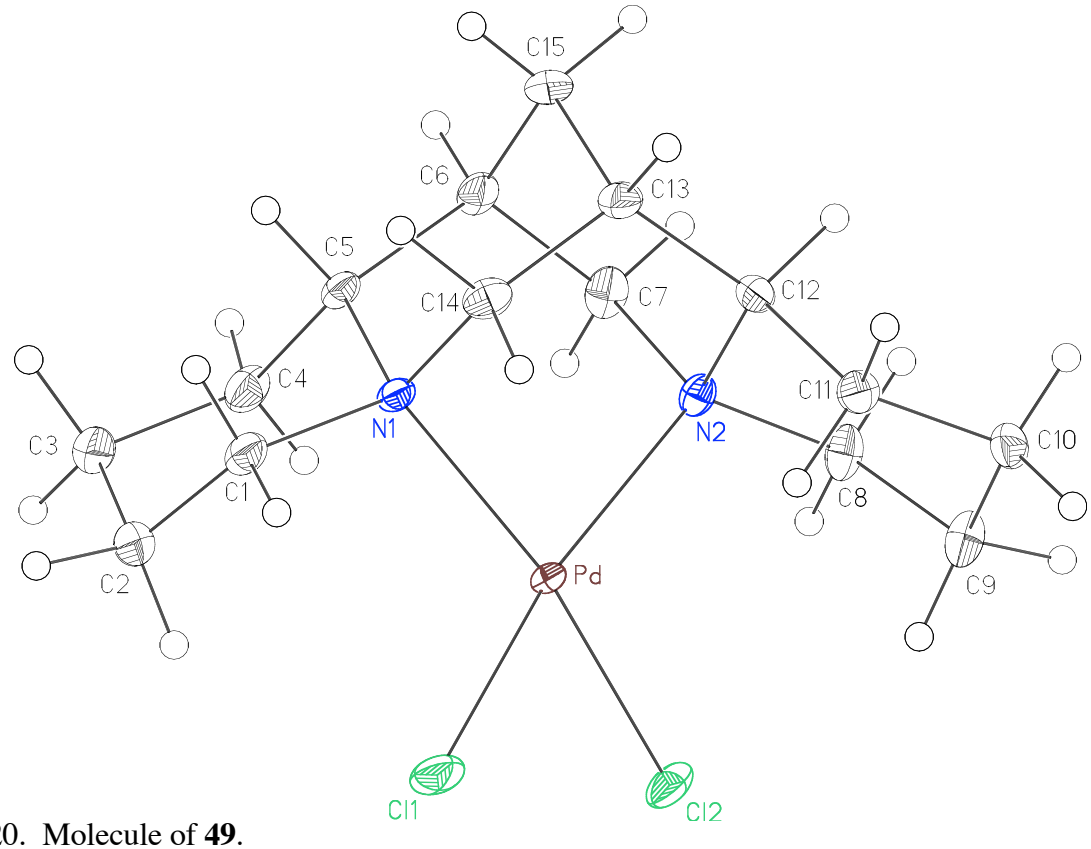

Figure S20. Molecule of **49**.

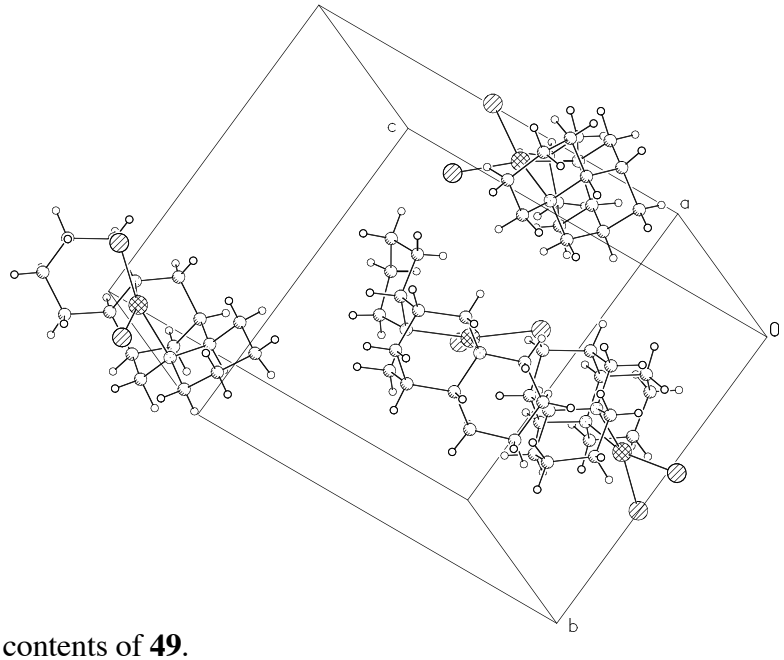

Figure S21. Unit cell contents of **49**.

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **49** (CCDC 223628). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd	8074(1)	9581(1)	9899(1)	9(1)
Cl(1)	5914(1)	10226(1)	10509(1)	25(1)
Cl(2)	8225(1)	8352(1)	11109(1)	17(1)
N(1)	7712(1)	10349(1)	8651(1)	10(1)
N(2)	10275(1)	9425(1)	9527(1)	11(1)
C(1)	6155(2)	10652(2)	8468(1)	16(1)
C(2)	5171(2)	9593(2)	8410(1)	20(1)
C(3)	5708(2)	8687(2)	7757(1)	20(1)
C(4)	7288(2)	8421(1)	7942(1)	16(1)
C(5)	8165(2)	9540(1)	7909(1)	11(1)
C(6)	9799(2)	9345(1)	7888(1)	14(1)
C(7)	10412(2)	8730(1)	8691(1)	15(1)
C(8)	11240(2)	8851(1)	10201(1)	16(1)
C(9)	11421(2)	9531(2)	11058(1)	17(1)
C(10)	11851(2)	10792(1)	10907(1)	15(1)
C(11)	10843(2)	11343(1)	10230(1)	14(1)
C(12)	10868(2)	10639(1)	9376(1)	12(1)
C(13)	10186(2)	11238(1)	8575(1)	15(1)
C(14)	8566(2)	11450(1)	8618(1)	14(1)
C(15)	10533(2)	10518(2)	7753(1)	18(1)

Table S14. Bond lengths [Å] and angles [°] for **49**. (CCDC 223628).

Pd-N(1)	2.1091(11)	C(8)-H(8A)	0.954(16)
Pd-N(2)	2.1271(12)	C(8)-H(8B)	0.960(18)
Pd-Cl(2)	2.3140(3)	C(9)-C(10)	1.519(2)
Pd-Cl(1)	2.3275(4)	C(9)-H(9A)	0.912(18)
N(1)-C(14)	1.493(2)	C(9)-H(9B)	0.98(2)
N(1)-C(1)	1.5118(18)	C(10)-C(11)	1.524(2)
N(1)-C(5)	1.5158(17)	C(10)-H(10A)	0.90(2)
N(2)-C(7)	1.4998(18)	C(10)-H(10B)	0.958(19)
N(2)-C(8)	1.5078(18)	C(11)-C(12)	1.522(2)
N(2)-C(12)	1.5166(19)	C(11)-H(11A)	0.984(19)
C(1)-C(2)	1.524(2)	C(11)-H(11B)	0.926(16)
C(1)-H(1A)	0.886(18)	C(12)-C(13)	1.530(2)
C(1)-H(1B)	0.896(18)	C(12)-H(12)	1.005(19)
C(2)-C(3)	1.519(2)	C(13)-C(14)	1.525(2)
C(2)-H(2A)	0.94(2)	C(13)-C(15)	1.527(2)
C(2)-H(2B)	0.95(2)	C(13)-H(13)	0.948(18)
C(3)-C(4)	1.523(2)	C(14)-H(14A)	1.002(18)
C(3)-H(3A)	0.96(2)	C(14)-H(14B)	1.035(18)
C(3)-H(3B)	0.97(2)	C(15)-H(15A)	0.914(19)
C(4)-C(5)	1.522(2)	C(15)-H(15B)	1.00(2)
C(4)-H(4A)	0.83(2)		
C(4)-H(4B)	0.960(18)	N(1)-Pd-N(2)	87.23(4)
C(5)-C(6)	1.534(2)	N(1)-Pd-Cl(2)	166.25(4)
C(5)-H(5)	0.993(15)	N(2)-Pd-Cl(2)	95.68(3)
C(6)-C(7)	1.515(2)	N(1)-Pd-Cl(1)	94.81(3)
C(6)-C(15)	1.524(2)	N(2)-Pd-Cl(1)	163.54(3)
C(6)-H(6)	0.951(17)	Cl(2)-Pd-Cl(1)	86.205(15)
C(7)-H(7A)	0.931(17)	C(14)-N(1)-C(1)	107.82(12)
C(7)-H(7B)	0.918(18)	C(14)-N(1)-C(5)	110.34(11)
C(8)-C(9)	1.521(2)	C(1)-N(1)-C(5)	105.75(11)

C(14)-N(1)-Pd	107.43(8)	H(7A)-C(7)-H(7B)	110.9(16)
C(1)-N(1)-Pd	114.30(8)	N(2)-C(8)-C(9)	114.61(12)
C(5)-N(1)-Pd	111.15(8)	N(2)-C(8)-H(8A)	108.4(10)
C(7)-N(2)-C(8)	106.63(11)	C(9)-C(8)-H(8A)	103.4(10)
C(7)-N(2)-C(12)	109.41(11)	N(2)-C(8)-H(8B)	107.5(11)
C(8)-N(2)-C(12)	106.75(11)	C(9)-C(8)-H(8B)	109.8(10)
C(7)-N(2)-Pd	110.42(9)	H(8A)-C(8)-H(8B)	113.2(14)
C(8)-N(2)-Pd	115.36(9)	C(10)-C(9)-C(8)	112.99(13)
C(12)-N(2)-Pd	108.11(8)	C(10)-C(9)-H(9A)	116.9(11)
N(1)-C(1)-C(2)	113.55(13)	C(8)-C(9)-H(9A)	103.0(11)
N(1)-C(1)-H(1A)	107.7(11)	C(10)-C(9)-H(9B)	108.9(12)
C(2)-C(1)-H(1A)	109.5(11)	C(8)-C(9)-H(9B)	109.3(12)
N(1)-C(1)-H(1B)	106.9(12)	H(9A)-C(9)-H(9B)	105.2(16)
C(2)-C(1)-H(1B)	112.8(12)	C(9)-C(10)-C(11)	109.62(12)
H(1A)-C(1)-H(1B)	106.1(16)	C(9)-C(10)-H(10A)	112.2(13)
C(3)-C(2)-C(1)	112.83(13)	C(11)-C(10)-H(10A)	107.2(13)
C(3)-C(2)-H(2A)	110.5(12)	C(9)-C(10)-H(10B)	113.3(12)
C(1)-C(2)-H(2A)	111.9(12)	C(11)-C(10)-H(10B)	108.3(12)
C(3)-C(2)-H(2B)	106.9(14)	H(10A)-C(10)-H(10B)	105.9(17)
C(1)-C(2)-H(2B)	110.0(15)	C(12)-C(11)-C(10)	109.79(12)
H(2A)-C(2)-H(2B)	104.1(18)	C(12)-C(11)-H(11A)	110.3(11)
C(2)-C(3)-C(4)	109.51(13)	C(10)-C(11)-H(11A)	111.9(11)
C(2)-C(3)-H(3A)	110.5(12)	C(12)-C(11)-H(11B)	107.6(12)
C(4)-C(3)-H(3A)	108.0(12)	C(10)-C(11)-H(11B)	109.8(11)
C(2)-C(3)-H(3B)	114.0(13)	H(11A)-C(11)-H(11B)	107.4(15)
C(4)-C(3)-H(3B)	109.6(13)	N(2)-C(12)-C(11)	110.83(11)
H(3A)-C(3)-H(3B)	104.9(17)	N(2)-C(12)-C(13)	112.49(12)
C(5)-C(4)-C(3)	109.83(13)	C(11)-C(12)-C(13)	115.15(12)
C(5)-C(4)-H(4A)	110.6(16)	N(2)-C(12)-H(12)	104.7(11)
C(3)-C(4)-H(4A)	113.9(16)	C(11)-C(12)-H(12)	102.6(11)
C(5)-C(4)-H(4B)	107.3(12)	C(13)-C(12)-H(12)	110.1(10)
C(3)-C(4)-H(4B)	113.6(12)	C(14)-C(13)-C(15)	109.20(13)
H(4A)-C(4)-H(4B)	101.3(19)	C(14)-C(13)-C(12)	116.51(12)
N(1)-C(5)-C(4)	110.18(11)	C(15)-C(13)-C(12)	108.23(13)
N(1)-C(5)-C(6)	112.27(11)	C(14)-C(13)-H(13)	102.9(11)
C(4)-C(5)-C(6)	113.98(12)	C(15)-C(13)-H(13)	114.0(11)
N(1)-C(5)-H(5)	107.3(9)	C(12)-C(13)-H(13)	106.0(11)
C(4)-C(5)-H(5)	106.9(9)	N(1)-C(14)-C(13)	112.95(12)
C(6)-C(5)-H(5)	105.8(9)	N(1)-C(14)-H(14A)	108.7(11)
C(7)-C(6)-C(15)	110.60(13)	C(13)-C(14)-H(14A)	116.2(11)
C(7)-C(6)-C(5)	115.02(12)	N(1)-C(14)-H(14B)	103.8(10)
C(15)-C(6)-C(5)	108.41(12)	C(13)-C(14)-H(14B)	113.9(11)
C(7)-C(6)-H(6)	106.6(11)	H(14A)-C(14)-H(14B)	99.9(14)
C(15)-C(6)-H(6)	107.0(10)	C(6)-C(15)-C(13)	106.02(12)
C(5)-C(6)-H(6)	108.9(11)	C(6)-C(15)-H(15A)	110.8(12)
N(2)-C(7)-C(6)	113.23(12)	C(13)-C(15)-H(15A)	109.4(12)
N(2)-C(7)-H(7A)	104.9(11)	C(6)-C(15)-H(15B)	108.0(13)
C(6)-C(7)-H(7A)	111.9(11)	C(13)-C(15)-H(15B)	111.3(12)
N(2)-C(7)-H(7B)	106.2(12)	H(15A)-C(15)-H(15B)	111.2(17)
C(6)-C(7)-H(7B)	109.5(12)		

X-ray crystallographic structure for **[(β-isosparteine)$PdCl_2$ (50)**. The crystallographic data for **50** have been deposited at the Cambridge Database (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 294052.

Crystal data and structure refinement for 50 (CCDC 294052).

Empirical formula	$C_{15}H_{26}N_2Cl_2Pd \bullet CH_2Cl_2$
Formula weight	496.60
Crystallization Solvent	Dichloromethane/pentane
Crystal Habit	Fragment
Crystal size	0.26 x 0.20 x 0.11 mm^3
Crystal color	Orange

Data collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 11706 reflections used in lattice determination	2.47 to 39.14°
Unit cell dimensions	a = 9.7607(3) Å b = 12.7153(4) Å c = 15.4067(5) Å
Volume	1912.13(10) $Å^3$
Z	4
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.725 Mg/m^3
F(000)	1008
Data collection program	Bruker SMART v5.630
θ range for data collection	2.08 to 40.49°
Completeness to θ = 40.49°	94.5 %
Index ranges	$-12 \le h \le 17$, $-22 \le k \le 22$, $-25 \le l \le 28$
Data collection scan type	ω scans at 5 ϕ settings
Data reduction program	Bruker SAINT v6.45A
Reflections collected	35980
Independent reflections	11125 [R_{int}= 0.0912]
Absorption coefficient	1.530 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.8498 and 0.6918

Structure solution and refinement

Structure solution program	Bruker XS v6.12
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	Bruker XL v6.12
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	11125 / 0 / 208
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.108
Final R indices [I>2σ(I), 7904 reflections]	R1 = 0.0466, *w*R2 = 0.0737
R indices (all data)	R1 = 0.0766, *w*R2 = 0.0788
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.001
Average shift/error	0.000
Absolute structure determination	Anomalous dispersion
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	2.815 and -2.630 $e.Å^{-3}$

Special refinement details

All prominent peaks in the final electron density difference Fourier map all lie near the metal center.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

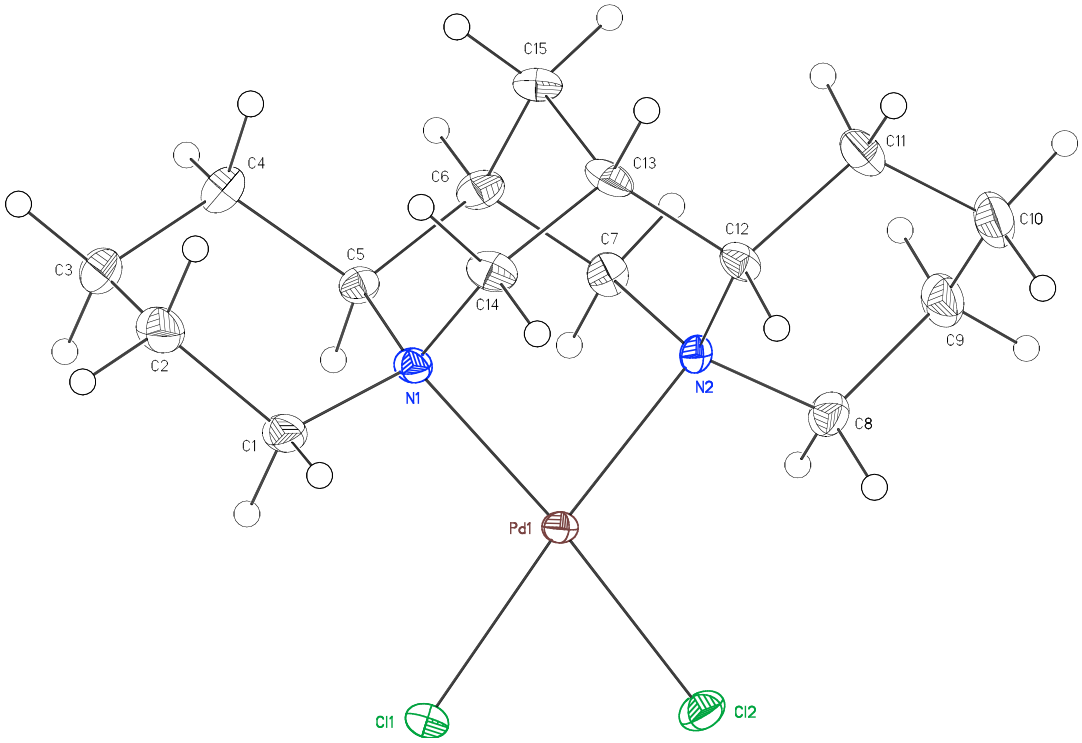

Figure S22. Molecule of **50**.

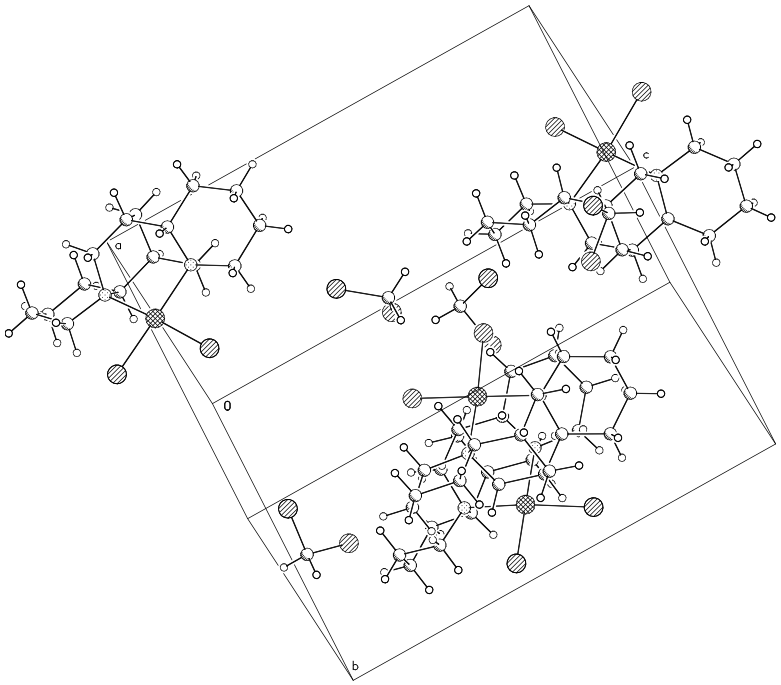

Figure S23. Unit cell contents of **50**.

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **50** (CCDC 294052). U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Pd(1)	4881(1)	2156(1)	9829(1)	10(1)
Cl(1)	4734(1)	554(1)	9114(1)	17(1)
Cl(2)	5018(1)	1099(1)	11053(1)	18(1)
N(1)	4943(3)	3067(1)	8668(1)	12(1)
N(2)	4881(3)	3606(2)	10536(1)	10(1)
C(1)	4896(4)	2372(2)	7869(2)	18(1)
C(2)	5211(3)	2926(2)	7018(2)	21(1)
C(3)	6655(3)	3363(2)	7057(2)	23(1)
C(4)	6732(3)	4144(2)	7809(2)	18(1)
C(5)	6297(3)	3657(2)	8687(2)	13(1)
C(6)	6265(3)	4529(2)	9378(2)	17(1)
C(7)	6208(3)	4133(2)	10316(2)	14(1)
C(8)	4870(4)	3398(2)	11498(2)	17(1)
C(9)	4676(3)	4375(2)	12058(2)	22(1)
C(10)	3336(3)	4922(3)	11835(2)	24(1)
C(11)	3360(3)	5186(2)	10876(2)	20(1)
C(12)	3639(3)	4234(2)	10284(2)	13(1)
C(13)	3746(3)	4621(2)	9340(2)	17(1)
C(14)	3719(3)	3764(2)	8653(2)	16(1)
C(15)	5064(3)	5271(2)	9211(2)	19(1)
Cl(3)	-896(1)	2192(1)	5659(1)	34(1)
Cl(4)	1894(1)	1994(1)	6342(1)	30(1)
C(16)	757(4)	1632(3)	5514(2)	29(1)

Table S16. Bond lengths [Å] and angles [°] for **50** (CCDC 94052).

Pd(1)-N(1)	2.1332(19)	C(1)-N(1)-C(5)	109.3(2)
Pd(1)-N(2)	2.1417(19)	C(14)-N(1)-Pd(1)	108.28(18)
Pd(1)-Cl(2)	2.3188(6)	C(1)-N(1)-Pd(1)	111.34(13)
Pd(1)-Cl(1)	2.3203(6)	C(5)-N(1)-Pd(1)	106.03(16)
N(1)-C(14)	1.488(4)	C(7)-N(2)-C(12)	113.71(18)
N(1)-C(1)	1.516(3)	C(7)-N(2)-C(8)	107.9(2)
N(1)-C(5)	1.520(4)	C(12)-N(2)-C(8)	110.0(2)
N(2)-C(7)	1.497(3)	C(7)-N(2)-Pd(1)	105.71(16)
N(2)-C(12)	1.502(3)	C(12)-N(2)-Pd(1)	109.04(16)
N(2)-C(8)	1.506(3)	C(8)-N(2)-Pd(1)	110.40(14)
C(1)-C(2)	1.519(3)	N(1)-C(1)-C(2)	115.10(19)
C(2)-C(3)	1.517(4)	C(3)-C(2)-C(1)	108.9(2)
C(3)-C(4)	1.528(4)	C(2)-C(3)-C(4)	108.3(2)
C(4)-C(5)	1.547(4)	C(3)-C(4)-C(5)	112.9(2)
C(5)-C(6)	1.538(4)	N(1)-C(5)-C(6)	110.6(2)
C(6)-C(15)	1.526(4)	N(1)-C(5)-C(4)	114.8(2)
C(6)-C(7)	1.532(4)	C(6)-C(5)-C(4)	108.8(2)
C(8)-C(9)	1.525(4)	C(15)-C(6)-C(7)	109.5(2)
C(9)-C(10)	1.521(4)	C(15)-C(6)-C(5)	110.2(2)
C(10)-C(11)	1.515(4)	C(7)-C(6)-C(5)	114.6(2)
C(11)-C(12)	1.540(4)	N(2)-C(7)-C(6)	113.1(2)
C(12)-C(13)	1.540(4)	N(2)-C(8)-C(9)	114.5(2)
C(13)-C(14)	1.519(4)	C(10)-C(9)-C(8)	110.6(3)
C(13)-C(15)	1.541(4)	C(11)-C(10)-C(9)	107.9(2)
Cl(3)-C(16)	1.777(4)	C(10)-C(11)-C(12)	114.0(3)
Cl(4)-C(16)	1.752(4)	N(2)-C(12)-C(13)	111.0(2)
		N(2)-C(12)-C(11)	114.1(2)
N(1)-Pd(1)-N(2)	87.63(7)	C(13)-C(12)-C(11)	108.6(2)
N(1)-Pd(1)-Cl(2)	174.44(7)	C(14)-C(13)-C(12)	115.3(2)
N(2)-Pd(1)-Cl(2)	94.93(6)	C(14)-C(13)-C(15)	108.1(3)
N(1)-Pd(1)-Cl(1)	94.60(5)	C(12)-C(13)-C(15)	110.5(2)
N(2)-Pd(1)-Cl(1)	175.87(7)	N(1)-C(14)-C(13)	113.8(2)
Cl(2)-Pd(1)-Cl(1)	83.16(2)	C(6)-C(15)-C(13)	106.74(19)
C(14)-N(1)-C(1)	108.1(2)	Cl(4)-C(16)-Cl(3)	112.21(18)
C(14)-N(1)-C(5)	113.84(18)		

NMR spectra for compounds reported in the text.

Figure S23. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of **[(sparteine)Pd(pyridine)Cl]$^{+}$SbF$_6^{-}$ (16)**.

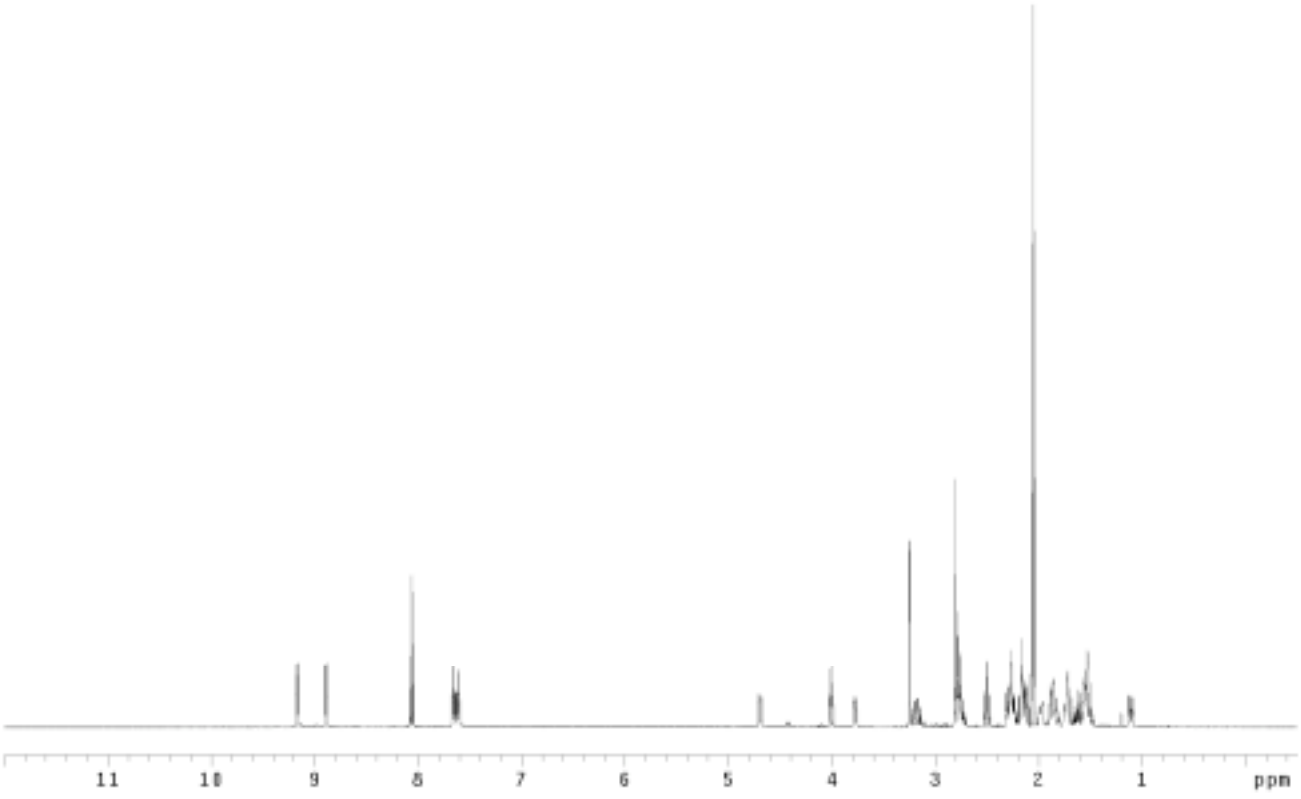

Figure S24. ^{13}C NMR spectrum (125 MHz, acetone-d_6) of **[(sparteine)Pd(pyridine)Cl]$^{+}$SbF$_6^{-}$ (16)**.

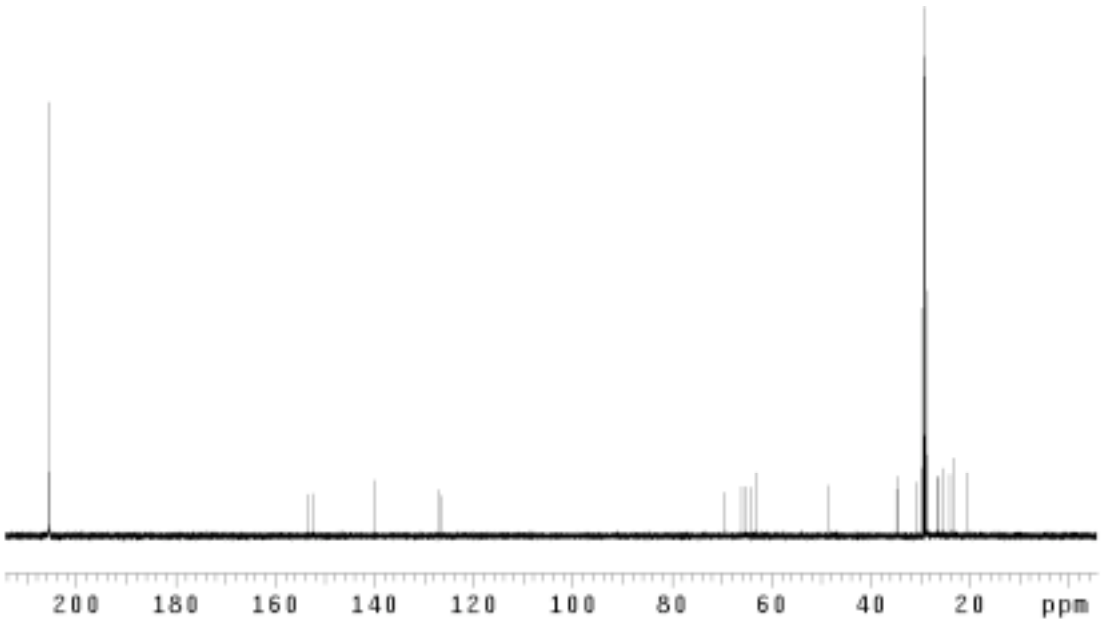

Figure S25. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of **[(sparteine)Pd(2-methylisoquinoline)Cl]$^{+}$SbF$_6^{-}$ (19/20)**.

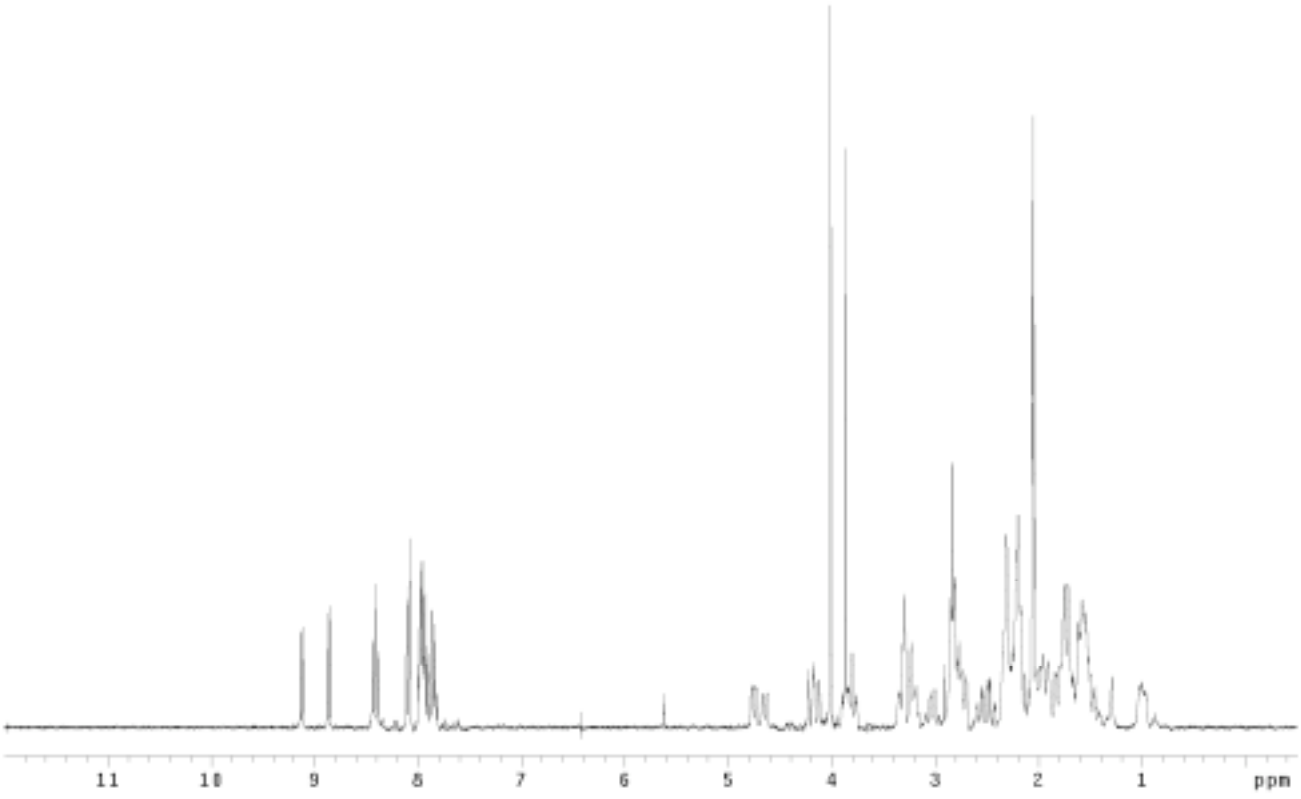

Figure S26. ^{13}C NMR spectrum (125 MHz, acetone-d_6) of **[(sparteine)Pd(2-methylisoquinoline)Cl]$^{+}$SbF$_6^{-}$ (19/20)**.

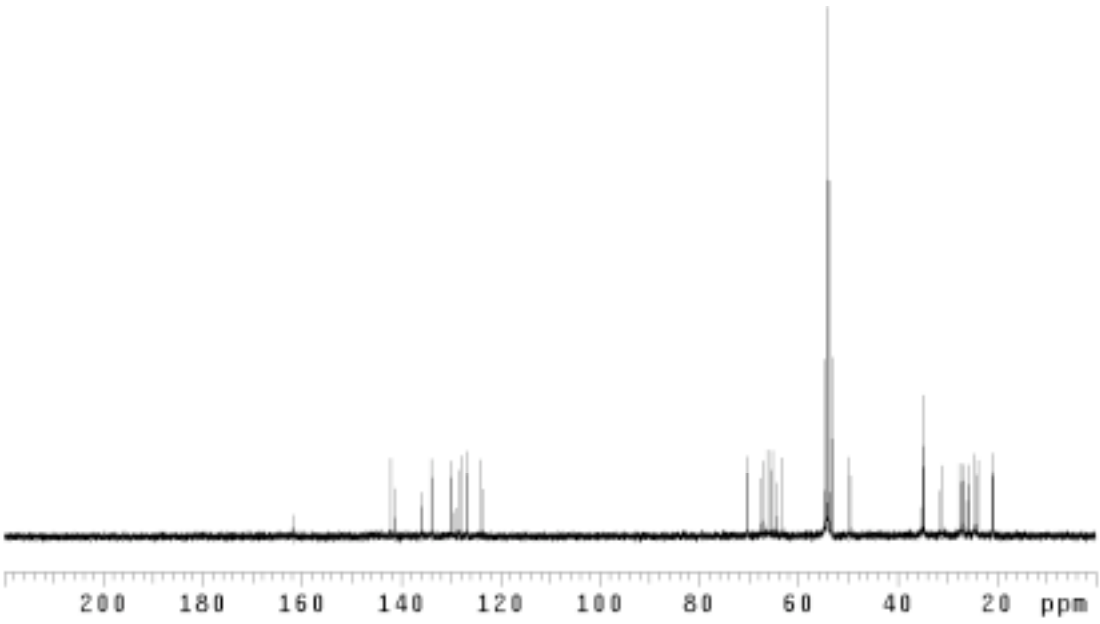

Figure S27. ^{1}H NMR spectrum (500 MHz, acetone-d_6) of **[(sparteine)Pd(2-mesitylpyridine)Cl]$^{+}$SbF$_6^{-}$ (24)**.

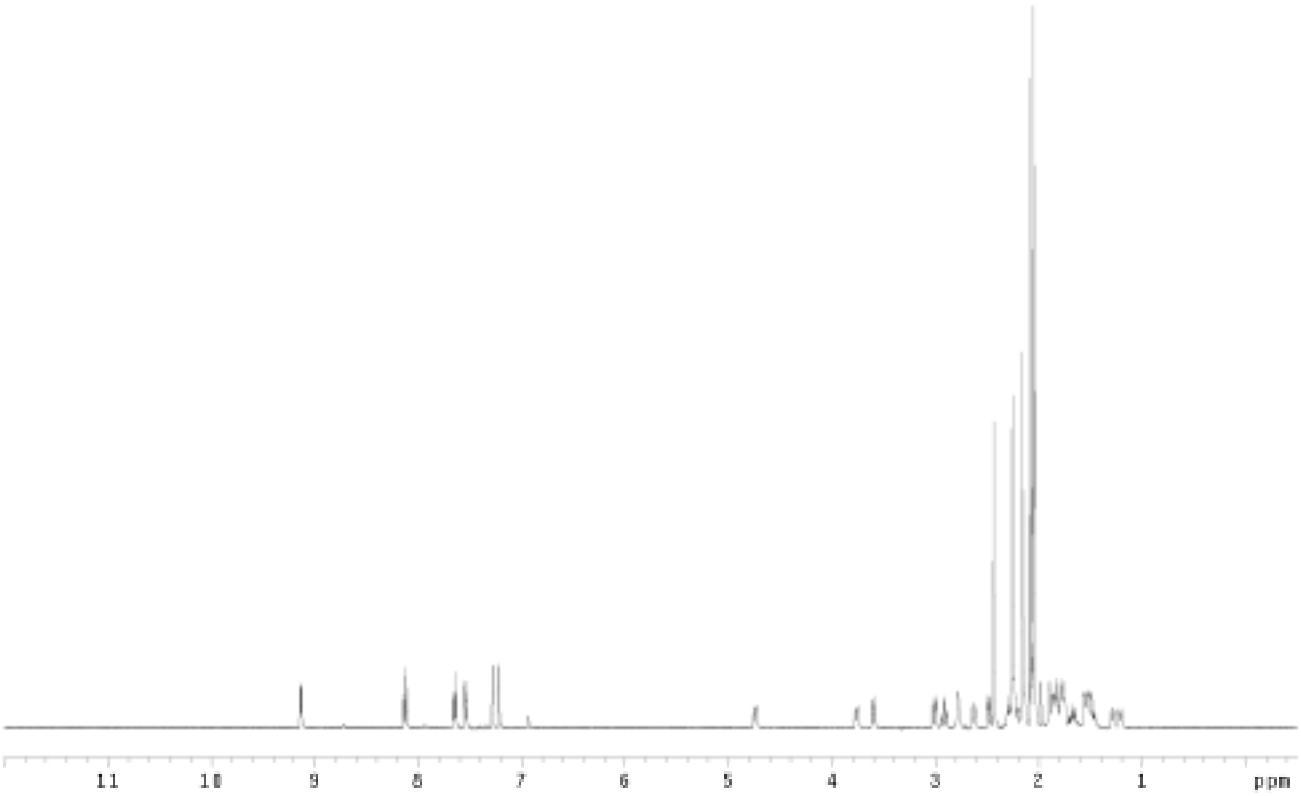

Figure S28. ^{13}C NMR spectrum (125 MHz, acetone-d_6) of **[(sparteine)Pd(2-mesitylpyridine)Cl]$^{+}$SbF$_6^{-}$ (24)**.

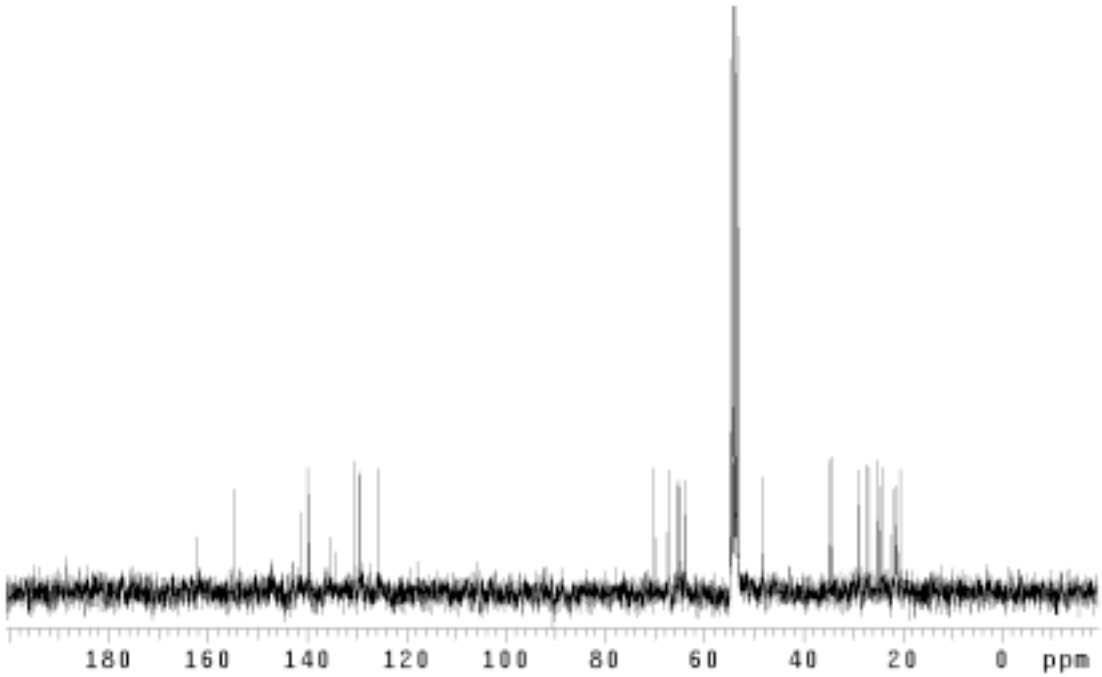

Figure S29. ^{1}H NMR spectrum (300 MHz, benzene-d_6) of **(sparteine)Pd(*S*-OCCF$_3$Ph)Cl (31)**.

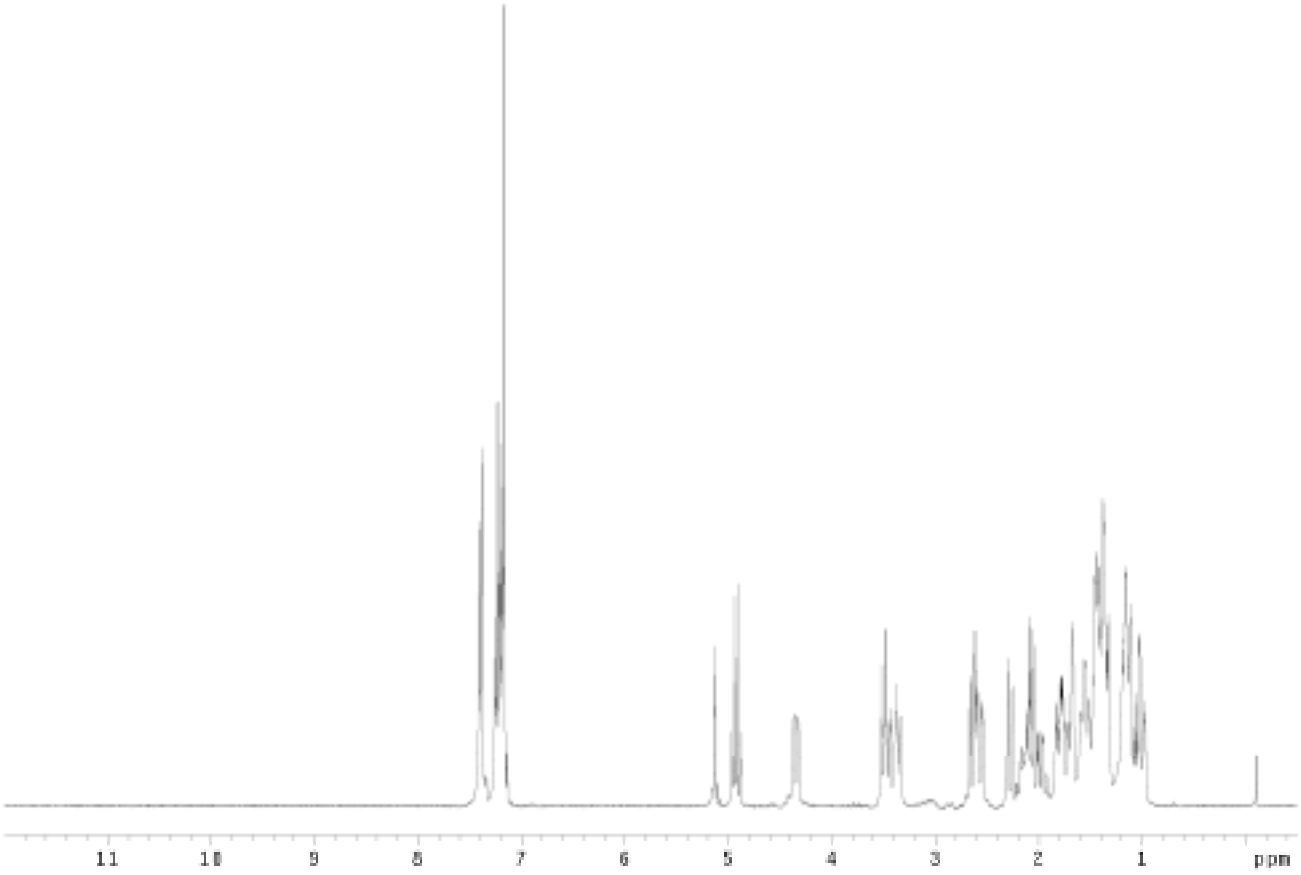

Figure S30. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of **(sparteine)Pd(*S*-OCCF$_3$Ph)Cl (31)**.

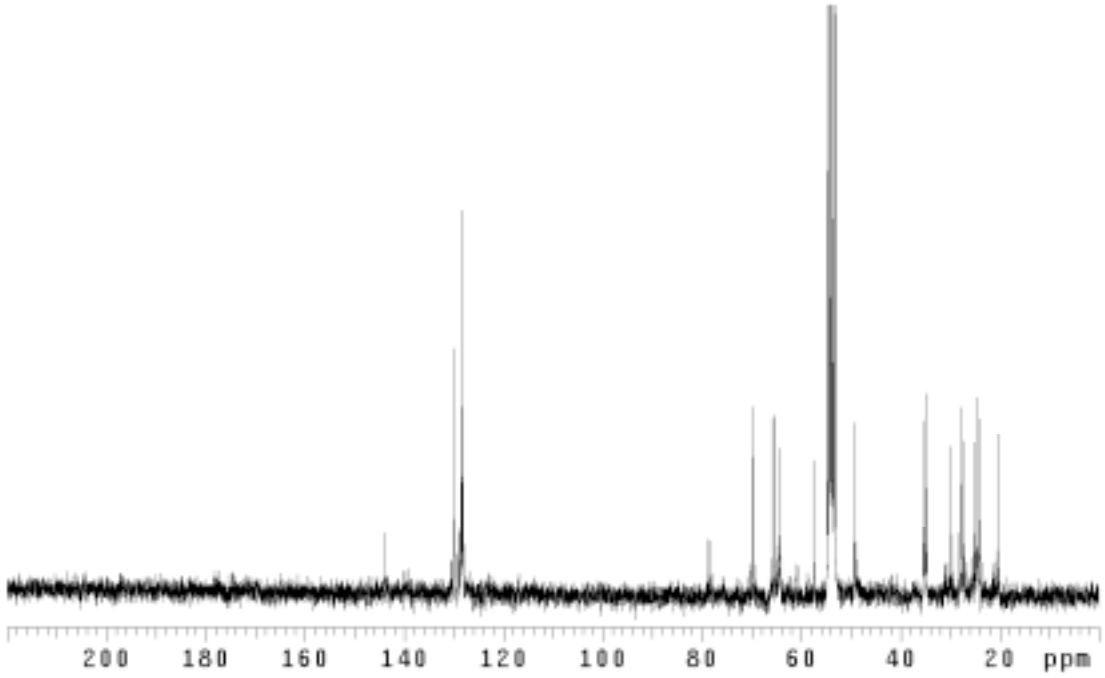

Figure S31. ^{19}F NMR spectrum (282 MHz, CD_2Cl_2 of **(sparteine)Pd(*S*-OCCF$_3$Ph)Cl (31)**.

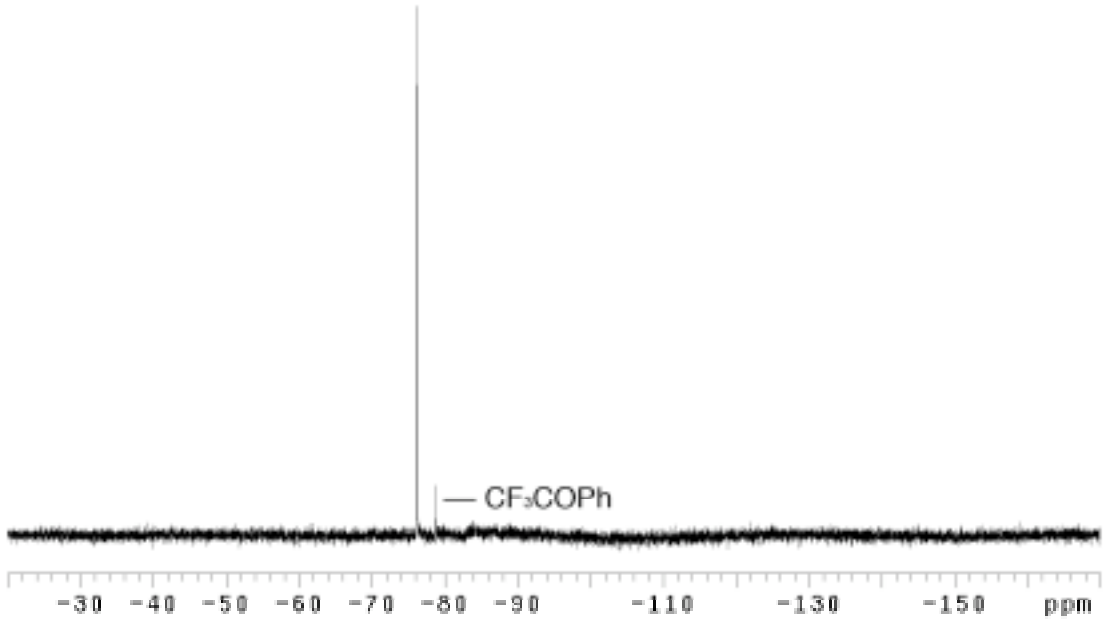

Figure S32. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **(sparteine)Pd(*R*-OCCF$_3$Ph)$_2$ (33)**.

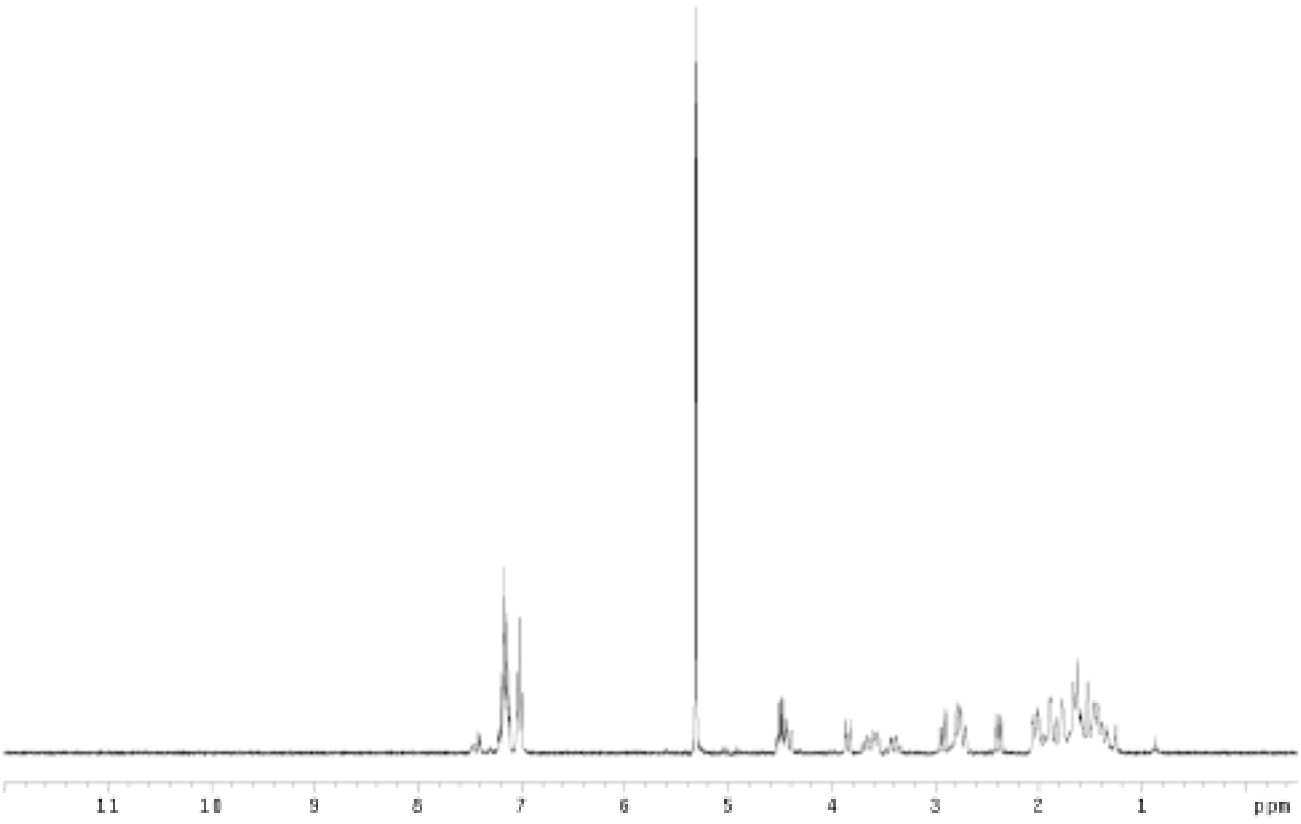

Figure S33. ^{13}C NMR spectrum (125 MHz, CD_2Cl_2) of **(sparteine)Pd(*R*-OCCF$_3$Ph)$_2$ (33)**.

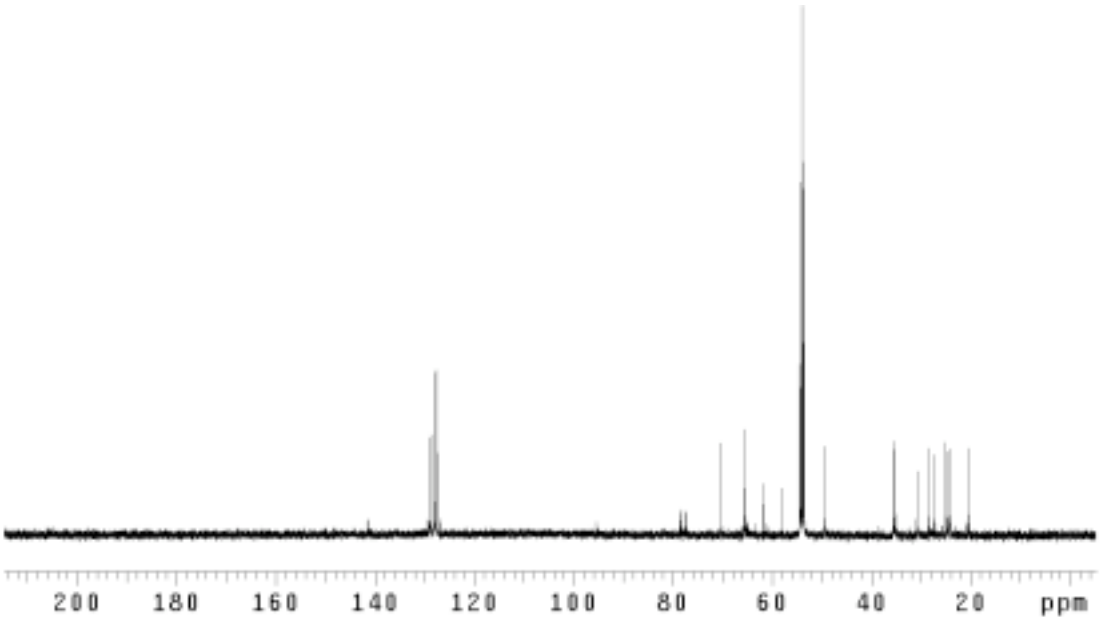

Figure S34. ^{19}F NMR spectrum (282 MHz, CD_2Cl_2 of **(sparteine)Pd(*R*-OCCF$_3$Ph)$_2$ (33)**.

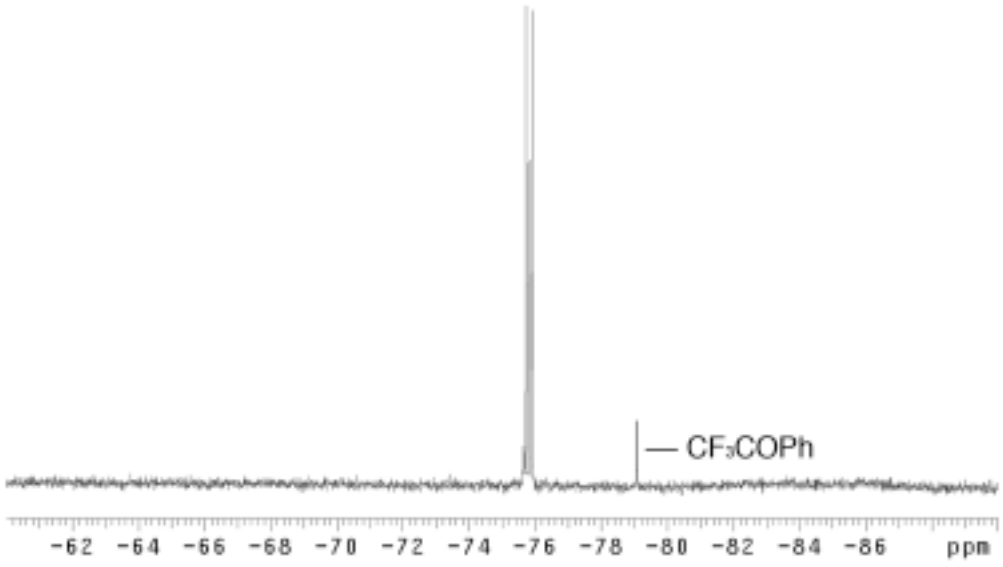

Figure S35. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **(sparteine)$PdBr_2$ (45)**.

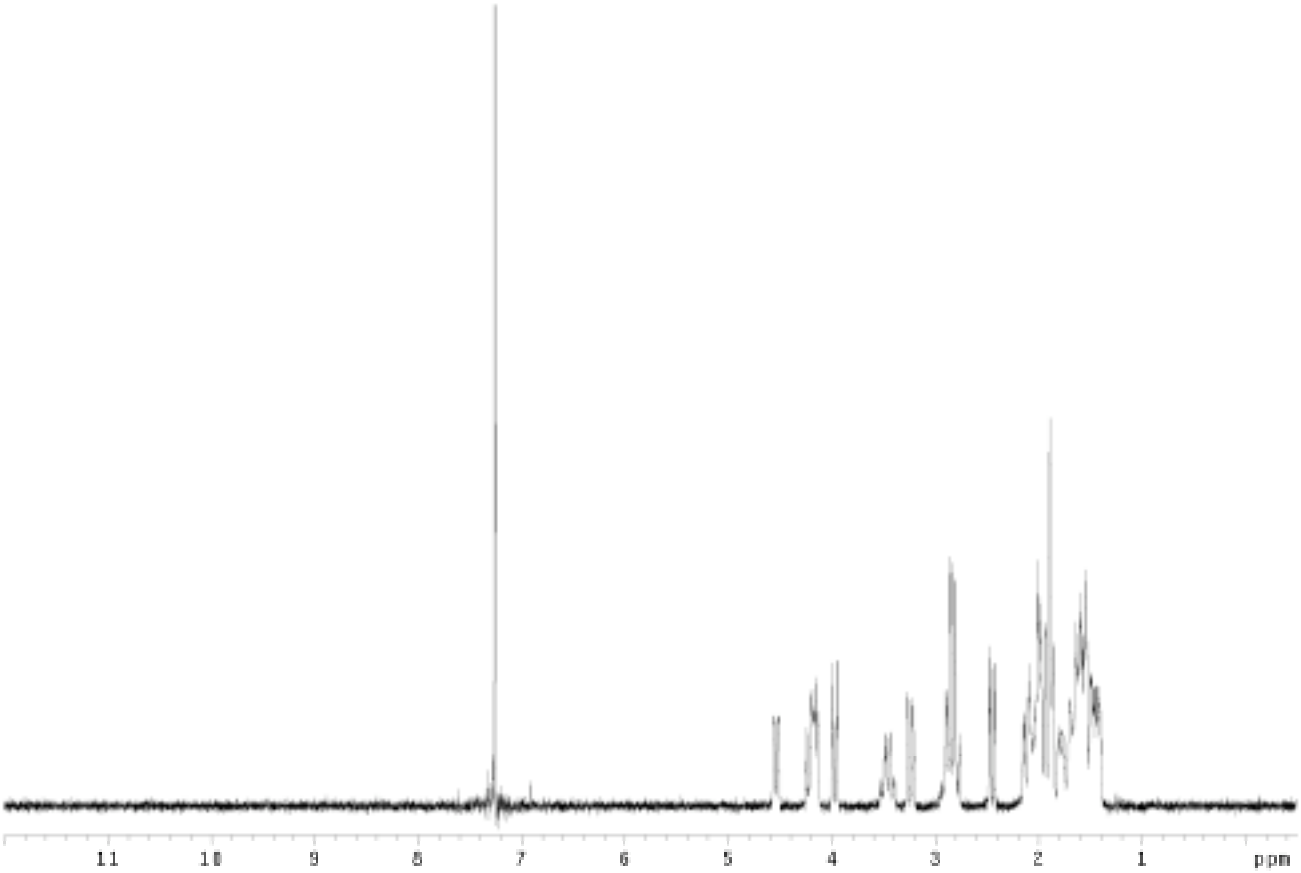

Figure S36. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of **(sparteine)$PdBr_2$ (45)**.

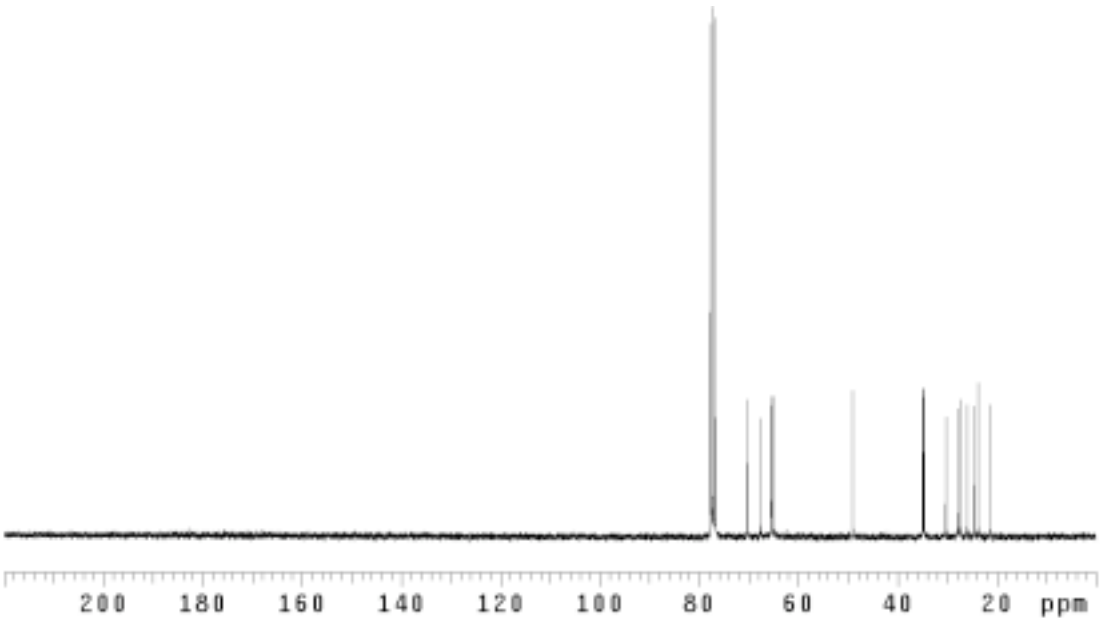

Figure S37. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of **didehydrosparteine (51)**.

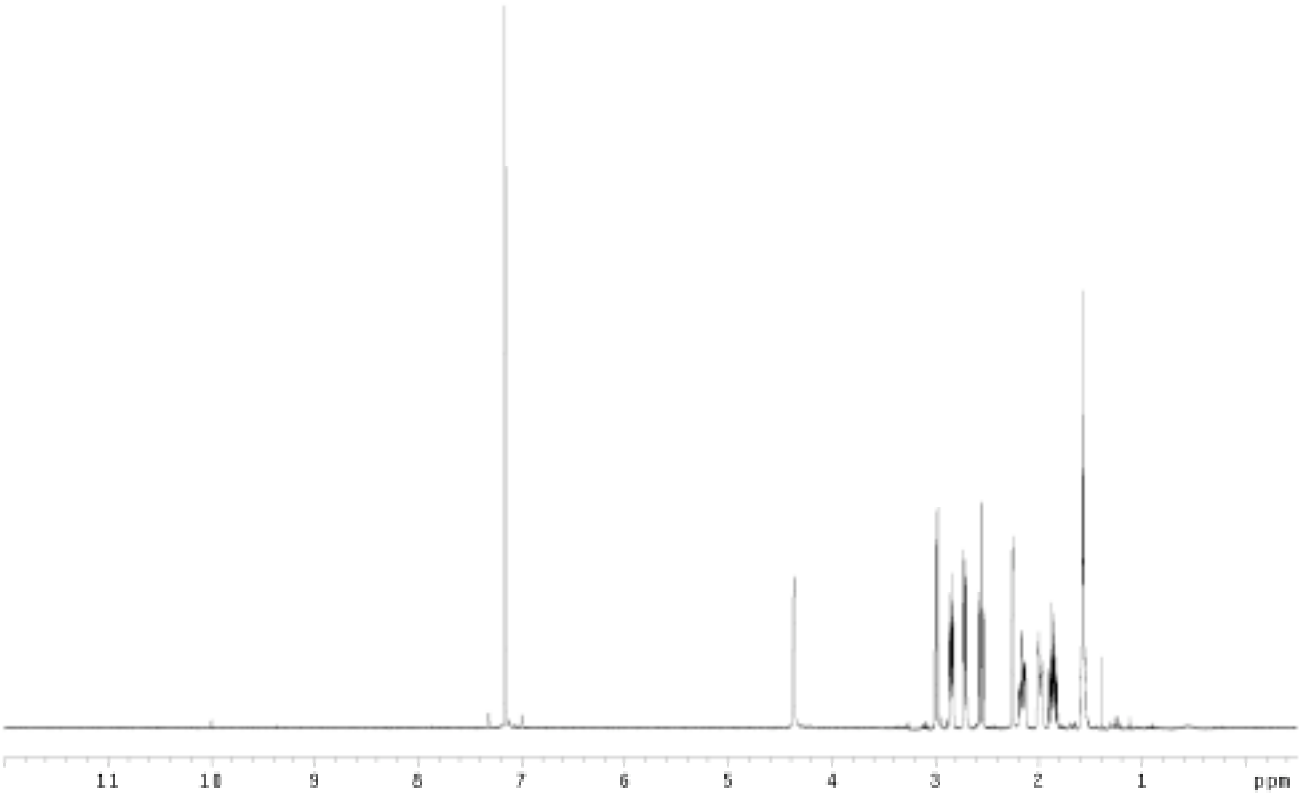

Figure S38. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **didehydrosparteine (51)**.

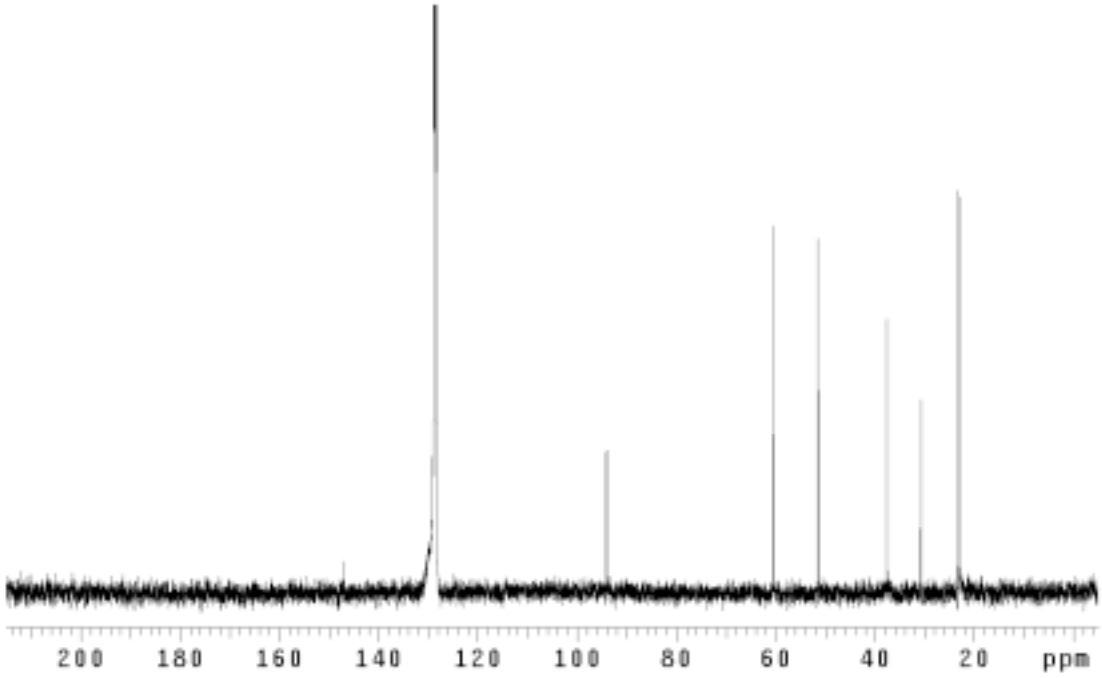

Figure S39. ^{1}H NMR spectrum (500 MHz, benzene-d_6) of **(–)-α-isosparteine (47)**.

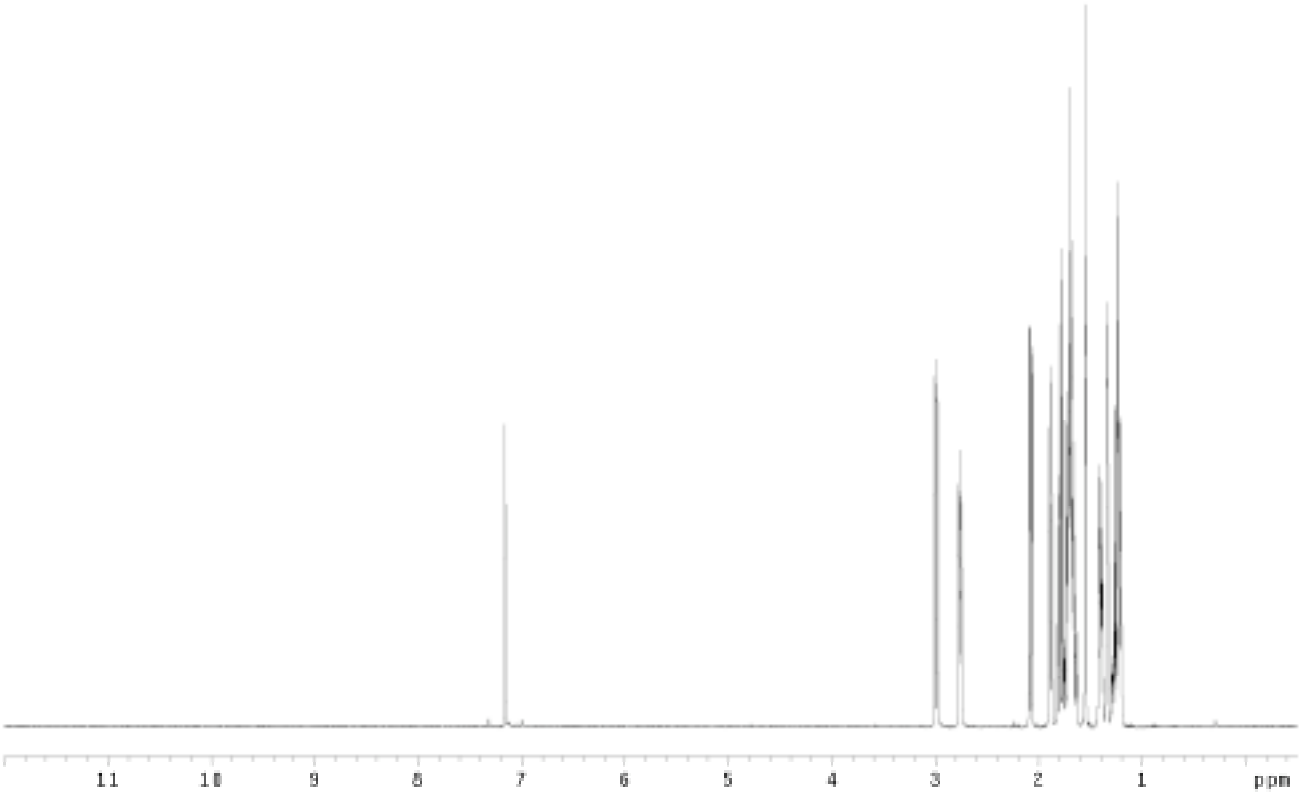

Figure S40. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **(–)-α-isosparteine (47)**.

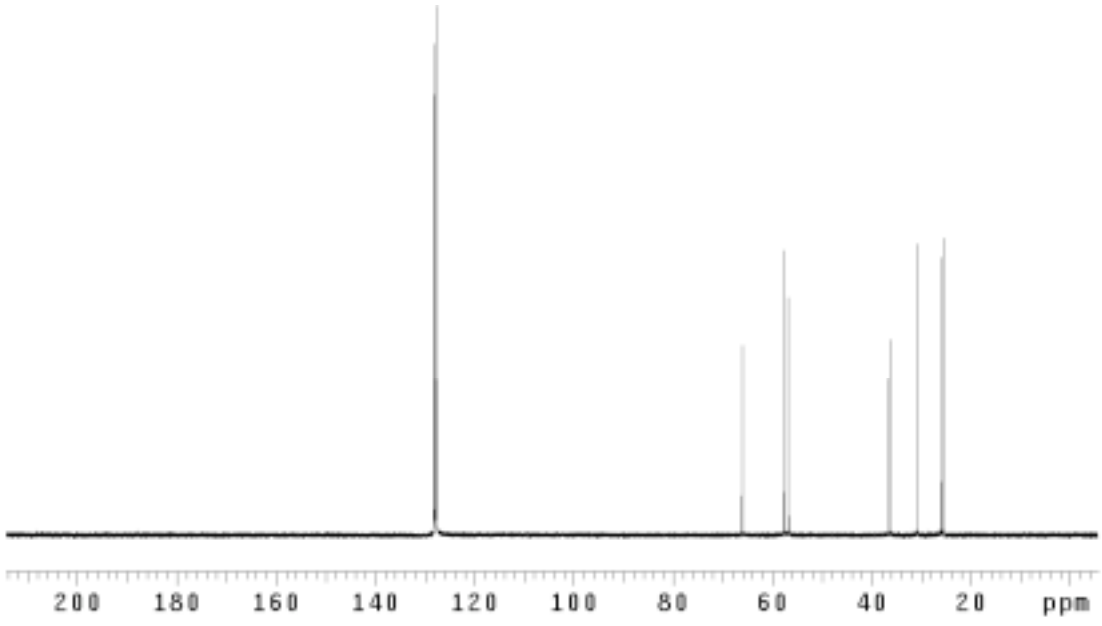

Figure S41. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **((–)-α-isosparteine)$PdCl_2$ (49)**.

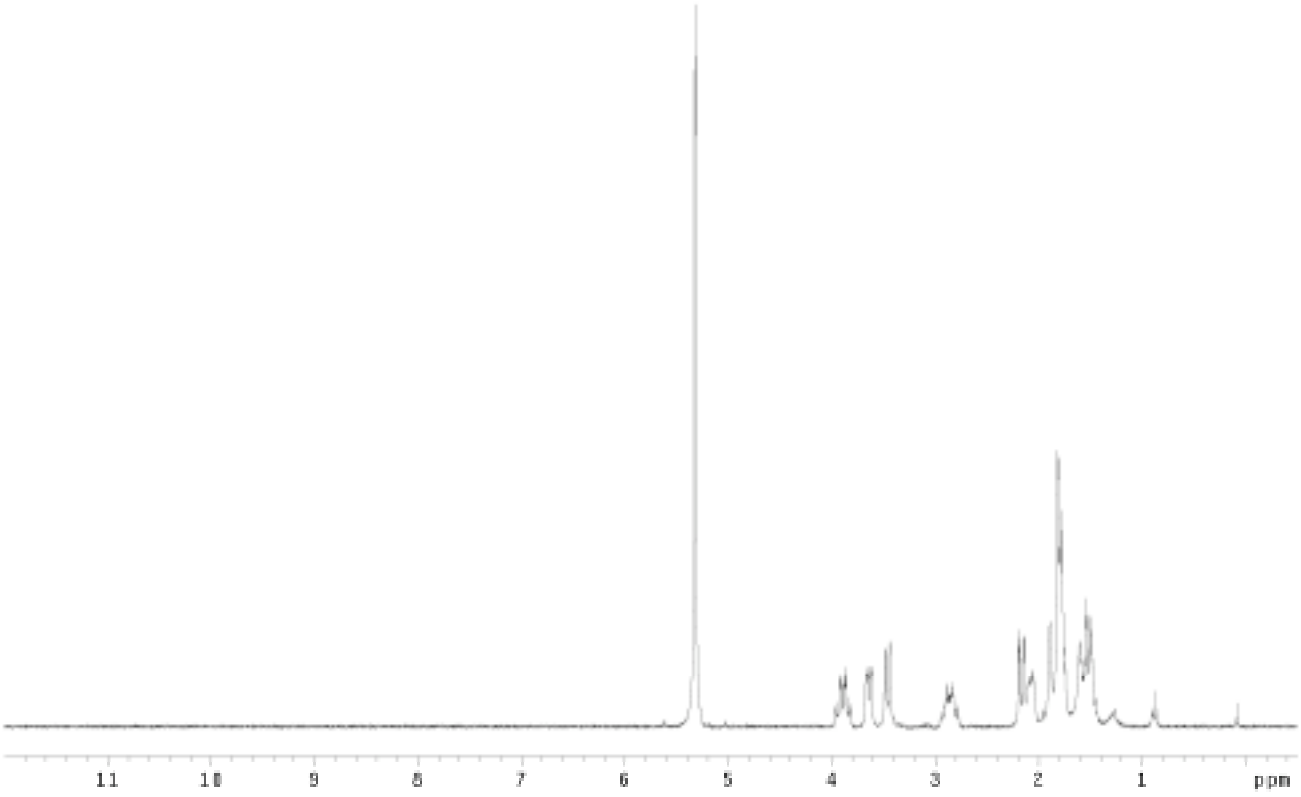

Figure S42. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of **((–)-α-isosparteine)$PdCl_2$ (49)**.

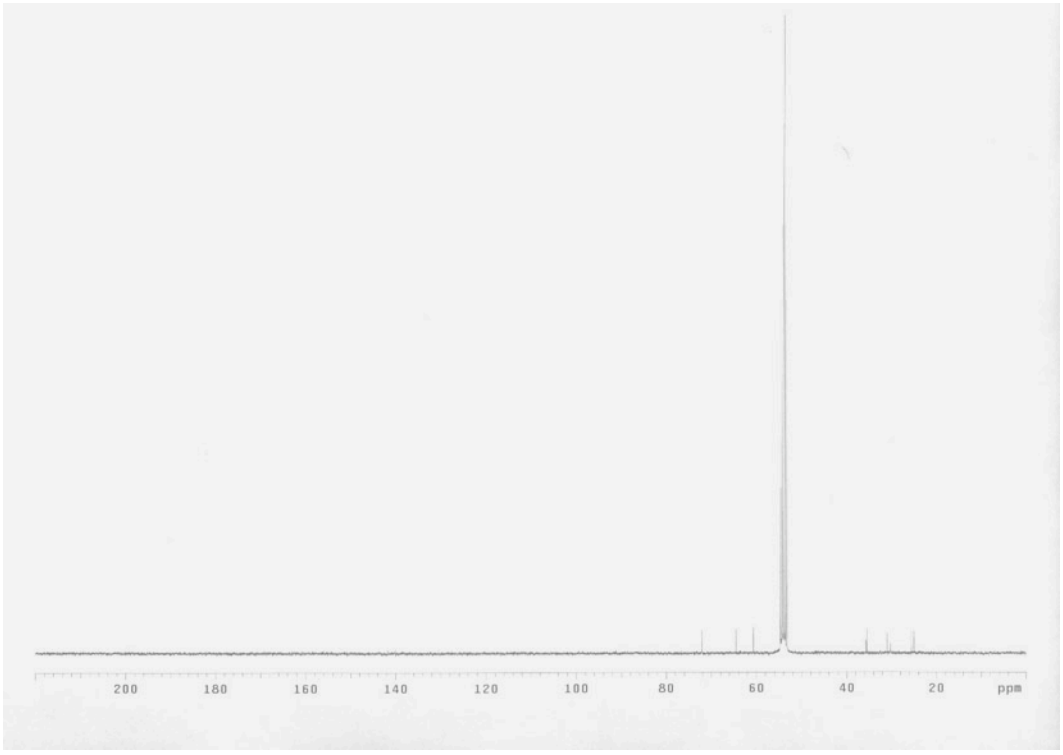

Figure S43. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **(+)-β-isosparteine (48)**.

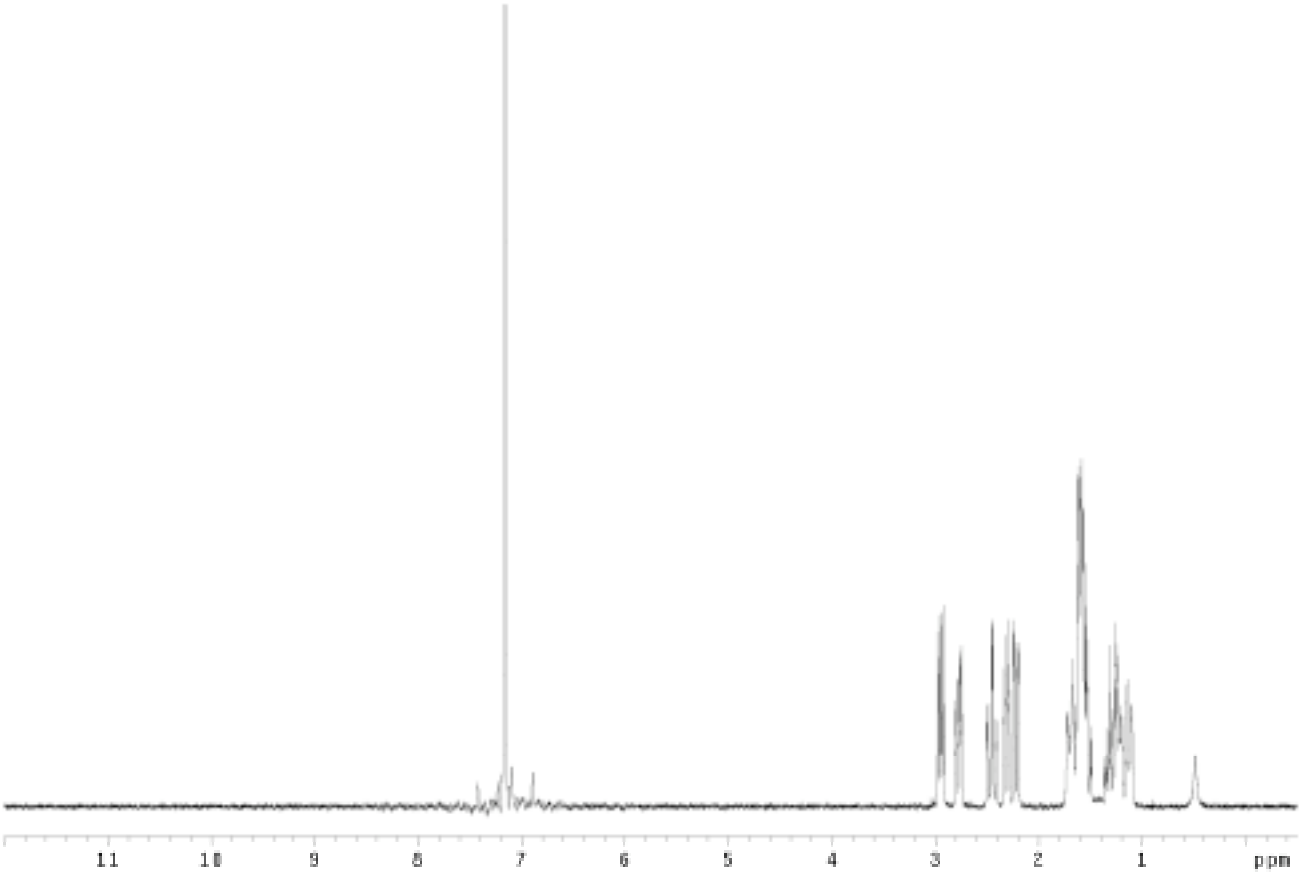

Figure S44. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **(+)-β-isosparteine (48)**.

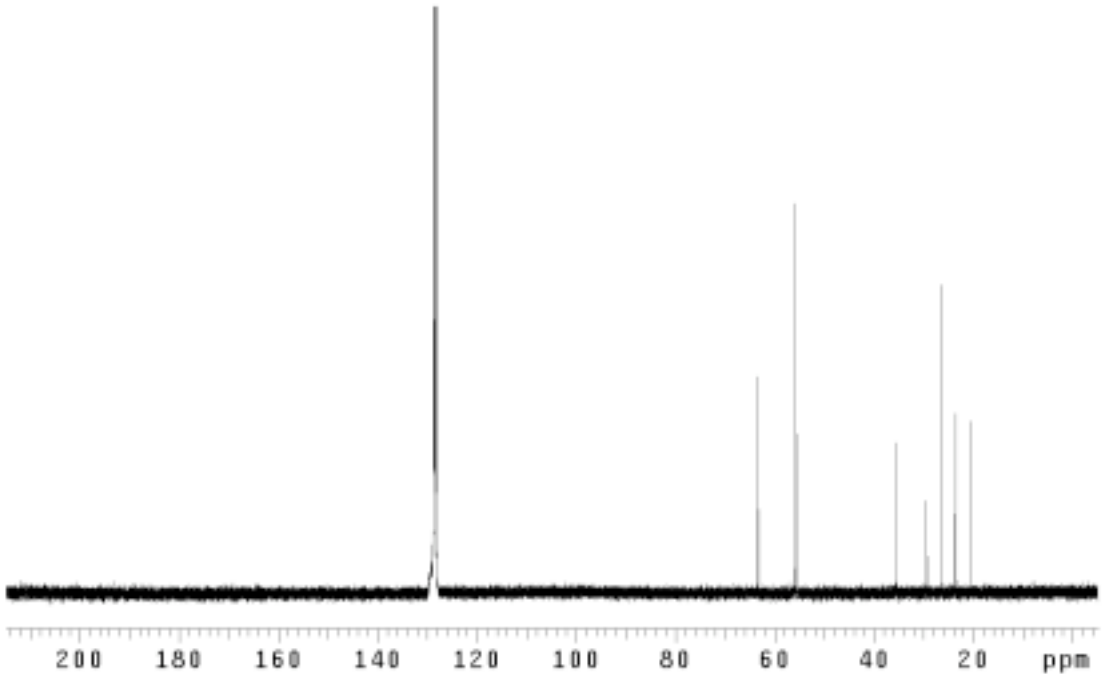

Figure S45. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of (**(+)-β-isosparteine)$PdCl_2$ (50**).

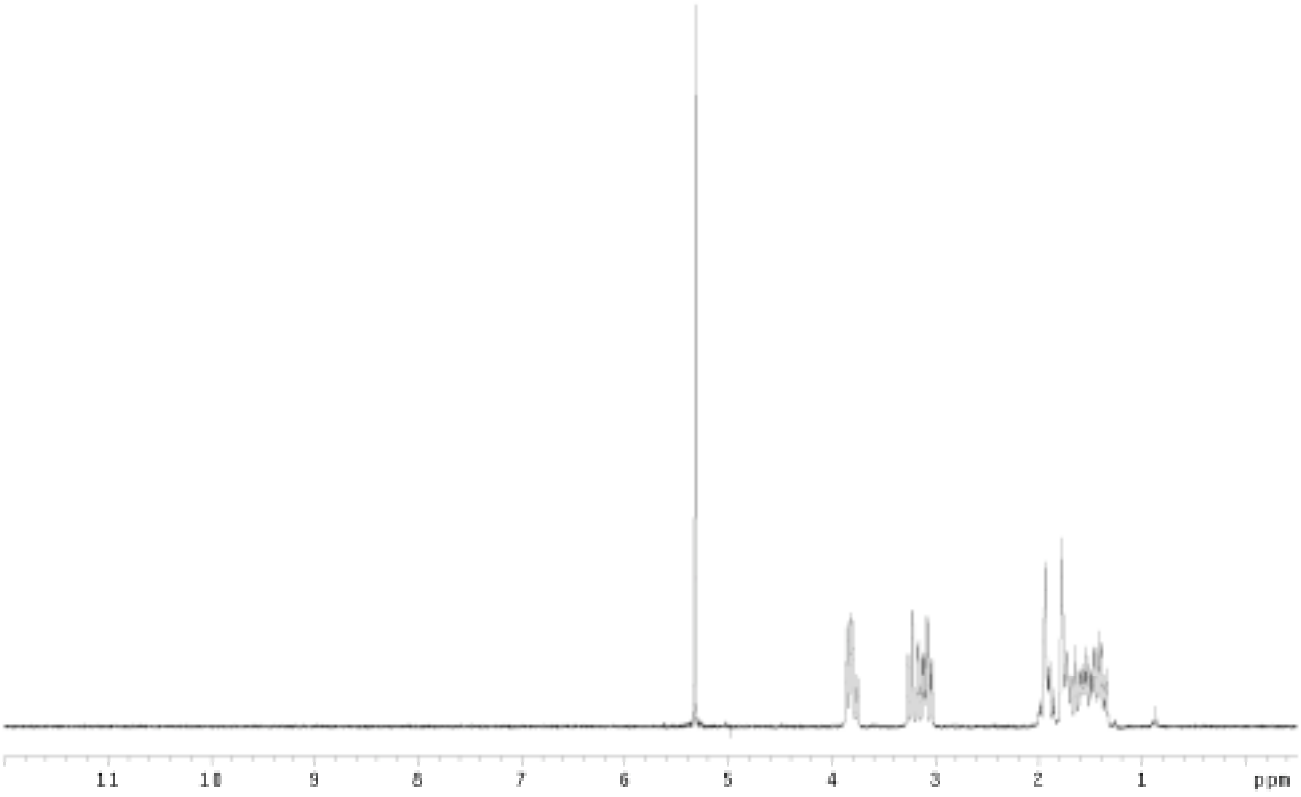

Figure S46. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of (**(+)-β-isosparteine)$PdCl_2$ (50**).